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SOME REACTIONS OF LUFFAMARIN

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The isolation of a crystalline substance from the seeds of *Luffa ægyptiaca* Mill. (Fam.: Cucurbitaceæ) was described in an earlier communication from this laboratory a few years ago.[1] The results of the experiments that we have performed on this substance have not been easy to interpret and hence their publication has been withheld so far. Recently a few papers have appeared in the literature describing the isolation of compounds having more or less the same melting point as ours from a variety of sources.[2–4] These papers contain data of a very superficial nature with regard to one or two properties of the substances discussed. In view of the appearance of these papers from other quarters, we consider it worthwhile to present our data without making any claims to correct interpretation.

Molecular formulæ having 15, 18, 19 and 32 carbon atoms in the molecule have been proposed by the different workers mentioned above for the compounds isolated by them. The data that we have makes it appear that the provisional formula $C_{20}H_{30}O_5$ may be a nearer representation of our substance.

To facilitate easy reference the compound isolated by us is now designated "Luffamarin". It has an acetoxyl group in its molecule. It gives an acetate which analyses for two acetoxyl groups. It also forms a benzoate and a 3:5-dinitrobenzoate. These point to the existence of one acylable hydroxyl group. The substance also forms an oxime and a 2:4-dinitrophenylhydrazone whose nitrogen contents indicate the presence of one ketonic group in the original molecule. Thus of the five oxygen atoms in the molecule four are accounted for, two by the acetoxyl group, one by the hydroxyl group and one by the ketonic group.

The function of the remaining oxygen is not quite obvious. The compound gives a positive Liebermann-Burchard reaction,[5–6] a positive reaction with antimony trichloride[7–8] and Shear's aniline-hydrochloric acid reaction.[9–10] These reactions are known to be answered by terpenoid compounds and by heterocyclic compounds containing oxygen as a hetero-atom. Hence it seems likely that the fifth oxygen exists in a hetero-ring.

Luffamarin reacts with bromine in carbon tetrachloride-chloroform mixture; quantitative titration indicates the addition of approximately two moles of bromine. The substance reacts with perbenzoic acid giving rise to a new compound whose analysis indicates the addition of two oxygen atoms. However, quantitative titration with perbenzoic acid indicated that only about 0·7 atom of oxygen was absorbed and the same value was obtained even on repetition. Luffamarin did not react with maleic anhydride when left with this reagent in benzene solution in the cold for 4 days.

Treatment with chromic acid (1 oxygen equivalent) at room temperature yielded a compound which analysed for $C_{20}H_{30}O_6$ or $C_{20}H_{28}O_6$. This compound yielded only a monodinitrophenylhydrazone. Oxidation with cold neutral potassium permanganate yielded a very small quantity of a neutral substance whose analysis indicated the addition of four hydroxyl groups to the molecule. This probably would indicate the presence of two double bonds.

Treatment with alkaline hydrogen peroxide gave an acid (probable formula $C_{13}H_{18}O_4$) as the main product. As minor products a neutral fraction (probable formula $C_{10}H_{12}O_2$?) and another substance soluble in sodium hydroxide but not in bicarbonate (probable formula $C_{10}H_{16}O_3$?) were obtained. The acid was characterized by the preparation of its methyl ester. When subjected to the action of acetic anhydride in the presence of pyridine, it yielded a new neutral compound which was free from acetoxyl group and whose formula indicated the removal of the elements of a molecule of water. The acid reacted with 2:4-dinitrophenylhydrazine to yield a hydrazone whose analysis indicated the existence of one carbonyl group.

Hydrolysis of luffamarin with weak alcoholic potash also resulted in clean degradation of the molecule. An acidic, a phenolic and a neutral fraction were obtained. Combustion values indicate the probable formulæ $C_7H_{10}O_2$, $C_{10}H_{16}O_3$ and $C_9H_{14}O_3$ respectively for them.

EXPERIMENTAL

Most of the substances described herein proved rather difficult to crystallize and in several cases they could be obtained only as microcrystalline powder.

Luffamarin was crystallised from chloroform-ether as colourless prisms melting at 180–82°. It is not soluble in 20% aqueous sodium hydroxide, cold or hot; but with concentrated alcoholic potash it gives a light reddish-yellow colour which gradually deepens on heating. It does not give any colour with alcoholic ferric chloride. It readily undergoes resinification with

either hot formic acid or hot alcoholic hydrochloric acid. It reduces Tollen's reagent in the cold. No green colour is produced when the substance is treated with concentrated sulphuric acid and gallic acid (absence of methylenedioxy group). [Found: C, 68·1; H, 8·9; $-COCH_3$, 11·4; M.W. (Rast.): 379, 388. $C_{20}H_{30}O_5$ (350·4) requires C, 68·6; H, 8·6; $-COCH_3$ (1), 12·3%.]

To a glacial acetic acid solution of luffamarin were added acetyl chloride and powdered zinc chloride and heated on a small open flame. Within a few minutes a yellow colour gradually changing to brownish-red was obtained (Tschugaieff reaction). In the Liebermann-Burchard reaction a green colour was obtained. On boiling the substance for half a minute with aniline and concentrated hydrochloric acid, a light red colour was obtained within half an hour, which deepened within 24 hours (Shear's aniline-hydrochloric acid reaction). No colour was obtained when a chloroform solution of the substance was treated with a solution of trichloroacetic acid (Rosenheim test). To a solution of the substance in absolute alcohol were added an absolute alcohol solution of *m*-dinitrobenzene and a solution of potassium hydroxide in absolute alcohol. A deep violet colour was obtained in a few minutes turning to blood-red after three hours (Zimmermann's reaction).[11] When luffamarin was moistened with hydrochloric acid containing ferric chloride and the resulting mixture evaporated to dryness, a violet residue was obtained.

When a small quantity of the substance was dissolved in a few ml. of chloroform and treated with a 25% solution of antimony trichloride in chloroform and left for two days, an orange–red layer separated at the bottom. The test was repeated with the addition of a small quantity of acetic anhydride before adding the reagent. A deep pink colour was obtained when left overnight.

Luffamarin acetate.—This was prepared by treating the substance in pyridine with acetyl chloride. The substance crystallized from dilute methanol as nodules and then from ether-petroleum ether as a microcrystalline powder melting at 129–30°. $[\alpha]_D^{27} = +2° \pm 1°$ ($c = 1·647$ in chloroform). [Found on substance dried in *in vacuo* for two hours at 90°: C, 66·2; H, 9·0; $-COCH_3$, 24·0. $C_{22}H_{32}O_6$ requires: C, 67·3; H, 8·2; $-COCH_3$ (2), 21·9%.]

Luffamarin benzoate.—This was prepared by treating the substance in absolute pyridine with benzoyl chloride. It crystallized from dilute methanol as colourless prisms melting at 140–42°. $[\alpha]_D^{28} = -48·6° \pm 3°$ ($c = 1·023$ in chloroform). (Found: C, 72·1; H, 7·6. $C_{27}H_{34}O_6$ requires; C, 71·3; H, 7·5%.)

Luffamarin 3: 5-*dinitrobenzoate*.—This was prepared on the same lines as above using 3: 5-dinitrobenzoyl chloride. It crystallized from dilute alcohol as colourless needles melting at 190–93°. $[\alpha]_D^{28} = +23{\cdot}8° \pm 2°$ ($c = 1{\cdot}249$ in chloroform). (Found: N, 5·5. $C_{27}H_{32}O_{10}N_2$ requires: N, 5·2%.)

Luffamarin oxime.—This was prepared by heating the substance in alcohol with a mixture of hydroxylamine hydrochloride and sodium acetate. The substance crystallized from benzene-acetone as colourless prisms melting at 187–89° (slight sintering at 150°). $[\alpha]_D^{27} = +38{\cdot}2° \pm 2°$ ($c = 1{\cdot}415$ in chloroform: acetone 4: 1). (Found: N, 4·7. $C_{29}H_{31}O_5N$ requires: N, 3·8%.)

Luffamarin 2: 4-*dinitrophenylhydrazone*.—This substance was prepared in the usual manner by treating luffamarin with the phenylhydrazine in alcohol with a trace of hydrochloric acid. It crystallized from alcohol as a reddish-yellow microcrystalline powder melting at 196–99°. (Found: N, 10·6. $C_{26}H_{34}O_8N_4$ requires: N, 10·6%.)

Bromine titration.—This was carried out by treating a known weight of the substance in a mixture of carbon tetrachloride and chloroform with excess of an approximately 2·5% solution of bromine in carbon tetrachloride, keeping the mixture in the dark for 2 hours and determining the excess of bromine in the usual manner by addition of potassium iodide and titrating with standard sodium thiosulphate solution. 200 mg. of the substance consumed bromine equivalent to 21·3 ml. of 0·1130 N thiosulphate (experiment 1) and 21·25 ml. of 0·1130 N thiosulphate (experiment 2) (Found: Number of double bonds: 2·1, in both experiments).

Oxidation with perbenzoic acid.—The substance (100 mg.) was dissolved in chloroform (5 ml.) and a chloroform solution of perbenzoic acid (10 ml.) was added. The solution was left in the ice-chest for 2 days with intermittent shaking. At the end of the period, a solution of potassium iodide (1 g.) and glacial acetic acid (2 ml.) in water (50 ml.) was added, the mixture thoroughly shaken and titrated against standard sodium thiosulphate solution. A blank experiment was also conducted. 100 mg. of the substance consumed perbenzoic acid equivalent to 3·2 ml. of 0·1130 N sodium thiosulphate solution (experiment 1) and 3·4 ml. of 0·1130 N sodium thiosulphate solution (experiment 2). [Found: No. of double bonds: 0·63 (experiment 1); 0·67 (experiment 2).]

The solution left at the end of the titration was transferred to a separating funnel, the lower chloroform layer was drawn off and the aqueous layer was extracted with chloroform (2 × 20 ml.). The mixed chloroform solution was diluted with three times its volume of ether, washed with 5%

sodium bicarbonate solution and then with water till neutral. It was dried over sodium sulphate, the solvents were removed and the residue was dissolved in benzene, concentrated and set aside, when a colourless sticky mass separated. This was dissolved in hot benzene, cooled and excess of petroleum ether was added when a white precipitate was obtained. It was filtered and washed with excess of petroleum ether, m.p. 108–12°/132–34°. $[\alpha]_D^{28} = +18{\cdot}9° \pm 4°$ ($c = 0{\cdot}9683$ in chloroform: acetone 4: 1). (Found: C, 62·9; H, 8·3. $C_{20}H_{30}O_7$ requires: C, 62·8; H, 7·9%.)

The same compound was obtained even when the solution, at the end of two days, was directly worked up without previous titration (mixed m.p.).

Chromic acid oxidation.—To a solution of the substance (0·2 g.) in glacial acetic acid (2 ml.) was added a 2% solution of chromium trioxide (2·1 ml.) in the same solvent (one atom of oxygen per mole of substance). The mixture was left for 3 hours at room temperature, diluted with dilute sulphuric acid (50 ml.), extracted with ether (4 × 30 ml.) and the combined ethereal extract washed with 2 N sodium carbonate solution and then with water till neutral. It was dried over sodium sulphate, the solvent was removed and the residue was purified by chromatography over alumina. By dissolving in ether and adding excess of petroleum ether, the substance was obtained as a powder melting at 108–11°. $[\alpha]_D^{28} = +4{\cdot}2° \pm 3°$ ($c = 1{\cdot}013$ in chloroform). (Found on sample dried *in vacuo* at 80° for two hours: C, 65·1; H, 8·2. $C_{20}H_{30}O_6$ requires: C, 65·6; H, 8·3%.)

The 2: 4-dinitrophenylhydrazone of the above oxidation product was prepared in the usual way. It crystallized from absolute alcohol as brownish red rods melting at 148–51°. (Found: N, 10·0. $C_{26}H_{34}O_9N_4$ requires: N, 10·3%.)

Permanganate oxidation.—To an acetone solution of the substance (0·25 g.) was added an aqueous solution of potassium permanganate till a permanent pink colour was obtained. Water was added and the solvent was removed under reduced pressure. Sulphur dioxide was passed through the resulting aqueous solution till the precipitated manganese dioxide went into solution. The solution was extracted with ether, the ethereal extract washed neutral and dried over sodium sulphate. Removal of the solvent left only a trace of residue. The aqueous layer left after ether extraction, when kept in the ice-chest for a month, deposited a small quantity of a crystalline material. This was filtered, washed and crystallized from methanol-ether when colourless needles melting at 318° were obtained (5 mg.). The substance was insoluble in 5% sodium hydroxide solution. (Found: C, 57·0; H, 8·5. $C_{20}H_{34}O_9$ requires: C, 57·4; H, 8·2%.)

Alkaline hydrogen peroxide oxidation of luffamarin.—To a solution of the substance (2·0 g.) in alcohol (60 ml.) were added a solution of potassium hydroxide (4 g.) in alcohol (20 ml.) and a solution of hydrogen peroxide, 100 vols. (24 ml.) and the mixture kept for 1 hour with occasional shaking. Next the solution was warmed until there was no more effervescence, neutralized with 1 : 1 hydrochloric acid to congo-red and the alcohol was removed under reduced pressure adding small quantities of water to keep the total volume approximately constant. The solution was extracted with ether (5 × 50 ml.). The combined ethereal extract was washed with water till neutral and extracted successively with 5% sodium bicarbonate solution (5 × 25 ml.) and 5% sodium hydroxide solution (3 × 20 ml.). The remaining ethereal layer was washed with water till neutral, dried and the solvent removed. The residue on crystallization from chloroform-ether yielded needles melting at 255–58° (0·02 g.). (Found: C, 71·7; H, 8·5%.)

The alkali-soluble fraction, recovered from the alkali extract, crystallized from chloroform-ether as feathery needles melting at 274–77° (5 mg.). The substance did not give any colour with alcoholic ferric chloride. (Found: C, 65·6; H, 8·5%.)

The acid recovered from the bicarbonate extract in the usual manner crystallized from ether-petroleum ether in nodules melting at 155–58° (0·7 g.). $[\alpha]_D^{28} = +94·2° \pm 3°$ ($c = 1·037$ in chloroform). [Found: C, 65·6; H, 7·6. M.W. (titration method): 256·2. $C_{13}H_{18}O_4$ (238·3) requires: C, 65·5; H, 7·6%.]

The methyl ester was prepared by treating an ethereal solution of the acid with excess of ethereal diazomethane. It was purified by dissolving in absolute ether and precipitating with excess of petroleum ether and thus obtained as a powder melting at 97–100° (decomp.). [Found on sample dried *in vacuo* at 60° for 2 hours: $-OCH_3$, 11·0. $C_{14}H_{20}O_4$ requires: $-OCH_3$ (1), 12·3%.]

The anhydro-acid was prepared by treating a solution of the acid (0·12 g.) in absolute pyridine (1·5 ml.) with acetic anhydride (0·75 ml.) and leaving at room temperature for 3 days. It crystallized from chloroform-ether in clusters of needles melting at 235–36°. (Found: C, 70·0; H, 8·0. $C_{13}H_{16}O_3$ requires: C, 70·9; H, 7·3%.)

The 2 : 4-dinitrophenylhydrazone of the acid was obtained from ether-petroleum ether as a micro-crystalline powder, m.p. 170–74°. (Found: N, 12·7. $C_{19}H_{22}O_7N_4$ requires: N, 13·4%.)

Alkali hydrolysis of luffamarin.—The substance (0·5 g.) was refluxed with N/5 alcoholic potash (50 ml.) for 1 hour. The resulting solution was worked up in the usual manner and the product separated into an acid fraction, a sodium hydroxide soluble fraction and a neutral fraction along usual lines.

The acid fraction (0·1 g.) was dissolved in chloroform, excess of benzene was added and concentrated to a small volume when a pasty mass separated. It was first purified through 5% A.R. sodium bicarbonate solution. By dissolving the dry substance in benzene and adding excess of petroleum ether a powder was obtained, m.p. 137–40°. $[\alpha]_D^{27} = +28° \pm 3°$ ($c = 0·995$ in chloroform). (Found: C, 66·7; H, 8·5. $C_7H_{10}O_2$ requires: C, 66·6; H, 8·0%.)

The sodium hydroxide soluble fraction was obtained as a powder by dissolving in benzene and adding excess of petroleum ether, m.p. 146–48°. It gave a violet-red colour with alcoholic ferric chloride and decolourized a solution of bromine in carbon tetrachloride. $[\alpha]_D^{28} = +14·9° \pm 4°$ ($c = 1·076$ in chloroform). (Found: C, 66·0; H, 8·3. $C_{10}H_{16}O_3$ requires: C, 65·2; H, 8·8%.)

The neutral fraction (0·21 g.) was purified through ether. After removal of the small amount (5 mg.) of an ether-insoluble impurity (colourless plates from benzene-methanol, m.p. 282–84°), the main portion (ether soluble) was purified by chromatography over alumina. It was obtained as a powder by dissolving in benzene and adding excess of petroleum ether, m.p. 156–59°. (Found: C, 62·6; H, 8·8. $C_9H_{15}O_3$ requires: C, 63·1, H, 8·8%.)

Summary

The crystalline substance obtained from the seeds of *Luffa ægyptiaca* Mill., now named "Luffamarin", has the probable molecular formula $C_{20}H_{30}O_5$. It contains an alcoholic hydroxyl group, a ketonic group and an acetoxyl group. The function of the remaining oxygen is not clearly known. It is probably present in a heterocyclic ring.

A number of derivatives and degradation products have been prepared and analysed.

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T.I.F.R. VAN DE GRAAFF ACCELERATOR

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1. Introduction

The Van de Graaff type electrostatic accelerator, in spite of its being in use for many years, retains its usefulness as a tool for research in low energy nuclear physics. A non-pressurized Van de Graaff accelerator cannot yield as high an accelerating voltage as a pressurized one; however, it is much simpler and considerably lower in cost. Work was therefore started on a non-pressurized accelerator at the Tata Institute of Fundamental Research, Bombay, with the two-fold objective of acquiring experience in the construction of electrostatic accelerators and carrying out a programme of research in low energy nuclear physics. The construction of the accelerator has been completed recently. Trial runs have shown that the accelerator, using a Philips Ion Gauge (PIG) type ion source, yields a maximum beam current of 10 μa. of H^+ and H_2^+ ions at a maximum energy of 300 Kev., which is the limit set by its present housing.

2. Constructional Details

(*a*) *High voltage generation and measurement.*—An overall view of the accelerator is shown in Fig. 1. The high voltage terminal is a hollow aluminium shell, the top half of which can be lifted up. Its maximum diameter is 5 ft. 9 in. It rests on a vertical insulating column, 6 ft. tall and 28½ in. diameter, consisting of twelve hollow perspex cylinders, separated by nickel-plated brass rings which define equipotential planes. The ground terminal, an aluminium shell which can be split into two halves, is placed on the floor. The charging is done by an endless, rubber impregnated canvas belt, manufactured by Arthur S. Brown Mfg. Co., Tilton, N.H., U.S.A. It is mounted on two pulleys, the lower one being movable for adjusting the belt tension. Positive charge is sprayed on the belt at the ground end from a series of needles connected to a 15 KV. variable D.C. power supply. The lower pulley is rotated at a speed of 4,200 r.p.m. by a 2 H.P. motor, thus

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moving the belt at 4,200 ft./min. Transfer of charge to the upper dome from the belt is accomplished by means of two rows of needles mounted inside the high voltage terminal. The belt is prone to absorbing moisture very readily, thus lowering its resistance considerably. In order to remove this moisture, the belt is heated while it is running by two 2·5 K.W. heaters placed

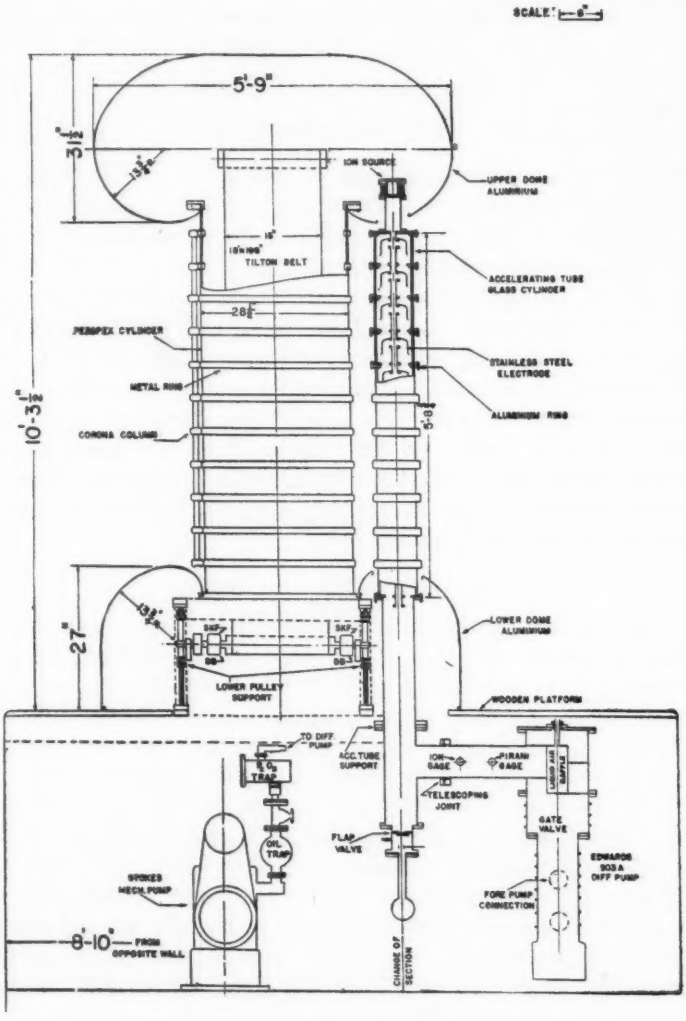

FIG. 1. T.I.F.R. Van de Graaff Accelerator

at the ground end. A second set of pulleys and corresponding motor have also been installed, so that charging can be done by two belts simultaneously if larger charging current is required.

Proper voltage distribution along the insulating column is achieved by means of ten corona needles, assembled and attached to the column as shown in Fig. 2. Brass rods, to which gramophone needles are soldered, are screwed in aluminium holders which are attached to the metal rings which define the equipotential planes. For varying the voltage distribution, each corona gap may be varied by screwing the needle in or out. During trial operation, each corona gap was set so as to spark over at a voltage of $\approx$50 KV across the gap. The corona gap thus served also as a protective device for the accelerating tube and the support column, by not allowing the voltage across any one section to exceed 50 KV.

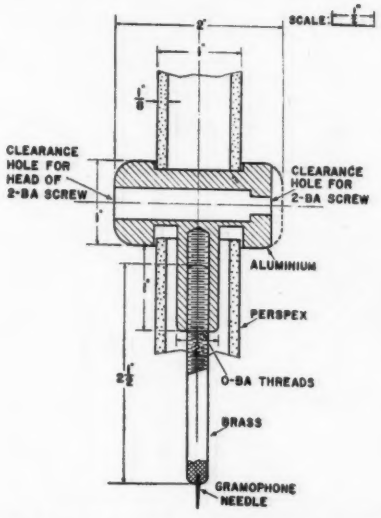

FIG. 2. T.I.F.R. Van de Graaff Accelerator Corona Needle Holders

Voltage on the high voltage terminal is measured by a generating voltmeter fixed to a vertical column near the accelerator. The signal of 200 cycles/second, generated in the voltmeter, is measured after amplification by an R–C coupled A.C. amplifier. A calibration curve was obtained by observing the signal for one suitable range of amplification, when the high voltage terminal was charged to known voltages by a 25 KV. power supply. Higher voltages could then be measured by using the same calibration curve,

but different ranges of amplification. Relative amplifications for different ranges were determined independently using known signal voltages. It is estimated that voltages measured in this manner are accurate to $\pm$ 15%.

(*b*) *Accelerating tube*.—For the design of a good accelerating tube, the following features must be considered: (i) Impedance to pumping must be small so that high vacuum can be maintained inside the tube, (ii) Electron loading must be prevented by minimising continuous paths for the electrons to travel up the tube, and (iii) Accelerating gaps must be electrically shielded, to stop any local field from affecting the beam.

The accelerating tube here consists of ten identical sections, one of which is illustrated in Fig. 3. The insulator is a Pyrex glass cylinder, of 7½ in. outer diameter and ⅜ in. wall thickness. Aluminium end plates, ½ in. thick, are attached to the two ends of the cylinder with cold setting araldite (Araldite Adhesive 103, CIBA Company, Bombay). The joint thus obtained is vacuum-tight and mechanically strong. Locally made neoprene O-rings are used

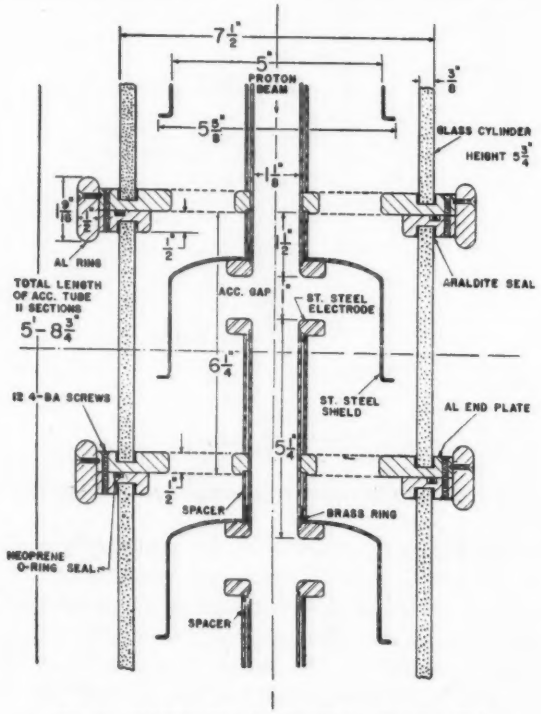

FIG. 3. T.I.F.R. Van de Graaff Accelerating Tube

between two sections for a vacuum seal. The electrode assembly, made of stainless steel, provides a uniform aperture of $1\frac{1}{8}$ in. diameter for the beam traversal and an accelerating gap of 1 in. per section. Aluminium rings with rounded ends cover the edges of end-plates at the joints between two sections. They are electrically connected to the metal rings of the support column, which define equipotential planes. Accelerating voltage is thus applied across each of the accelerating gaps.

(*c*) *Ion source and control system.*—A Philips Ion Gauge (PIG) type of ion source is used because it is extremely rugged and capable of giving large beam currents. The design is shown in Fig. 4. In a stainless steel chamber, of $1\frac{5}{8}$ in. inner diameter, a Philips type discharge is produced. An axial magnetic field is obtained by using a cylindrical permanent magnet and cylindrical pole pieces of iron. The anode is a ring of $\frac{1}{4}$ in. diameter

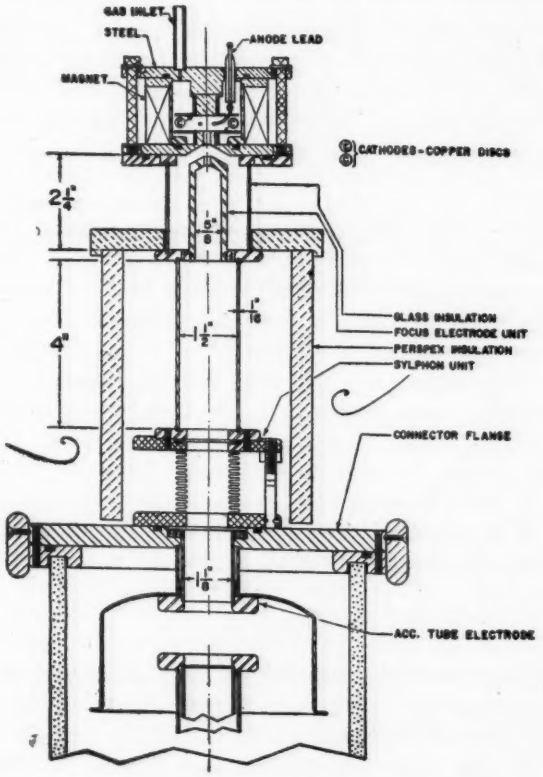

FIG. 4. T.I.F.R. Van de Graaff Accelerator Ion Source

made from 1/16 in. diameter copper wire. The ions produced come out from a 3/16 in. diameter hole in the lower pole face which is also the lower cold cathode. The emerging ion beam is then focussed by the focus electrode.

Anode and focus voltages are supplied, respectively, by 5 KV. and 25 KV. D.C. power supplies, situated on a platform inside the high voltage shell. Power is obtained from a 1 K.W., 1,600 cps. self-exciting generator, driven by a V-belt connected to the upper charging belt pulley. In order to vary the voltages from ground, power supply variacs are coupled to perspex tubes of 1 in. outside diameter, which go down to the ground end, where they are coupled to geared down reversible motors. These motors can be operated in either direction by means of spring switches on the control panel, thereby varying the voltages as desired. Control rod positions are remotely indicated by using potentiometers attached to them at the ground end.

Hydrogen gas to the ion source is supplied from a gas tank situated at the ground end and connected to the ion source through a garflex tubing. Gas flow is adjusted by means of two needle-valves, one of which can be controlled from the ground. This control and its indication are achieved by means of arrangements similar to those used for ion source voltage controls.

(*d*) *Vacuum system.*—The pumping system is situated in the experimental pit situated below the accelerator, as shown in Fig. 1. Edwards 903 A diffusion pump connected to a Stokes microvac model F mechanical pump through a P_2O_5 moisture trap, is used for obtaining high vacuum. Ion source, accelerating tube and its support tube made of brass are pumped through a liquid air baffle and a gate valve. Pumping speed of the diffusion pump with the gate valve attached is 900 litres/second at a pressure of 1×10^{-5} mm. of Hg. Pressure measurement up to 10^{-3} mm. of Hg is done by an Edwards Pirani Gauge; pressures lower than 10^{-3} mm. of Hg are measured by an Edwards ionization gauge. With the gas flow to the ion source closed off, a pressure of 1×10^{-5} mm. of Hg can be obtained in about two hours. After prolonged pumping, a pressure of 7×10^{-6} mm. can be obtained.

3. OPERATION

After pumping down the accelerating tube and drying the belt, high voltage shell is charged up and the ion source controls are adjusted to yield a focussed beam spot of $\approx \frac{1}{4}$ in. diameter on a piece of quartz situated at the ground end. For measuring the ion beam current on a microammeter quartz is rotated out of the beam path and replaced by a current collector.

The ion beam current consists of protons as well as molecular hydrogen ions. Without a magnetic analyser, it is difficult to know the percentage of each component. Operational characteristics of the accelerator at two different accelerating voltages are given in Table I.

TABLE I

Accelerating voltage ..	120 KV.	300 KV.
Ion beam current ..	40 μa.	9 μa.
Pressure ..	3×10^{-5} mm. of Hg	$4{\cdot}2\times10^{-5}$ mm. of Hg
Ion source anode voltage	$\approx$ ·4 KV.	$\approx 1{\cdot}5$ KV.
Ion source focus voltage	$\approx$ 6 KV.	$\approx$ 8 KV.

The beam current is steady and it can be maintained at a fixed value by occasional manual adjustment of controls. The accelerating voltage tends to drift slowly until a temperature equilibrium is established and the charging belt is thoroughly dry; however, this can be compensated for by adjusting the charging voltage. There is periodic variation of accelerating voltage due to oscillations of the charging belt. It is planned to install a voltage stabilizing system for correcting such voltage variations.

4. Concluding Remarks

Under ideal conditions of operation, upper limit of the accelerating voltage of a non-pressurized Van de Graaff accelerator is set by the insulating components of the machine. In the present case, however, corona current losses from the high voltage shell are high, since the shell is less than 4 ft. from the sides of the room. High humidity in the room, not an unusual occurrence in Bombay, increases the surface leakage on insulators. As a result, a large fraction of the charge carried up by the belt is drained away and the attainable accelerating voltage is low.

In order to increase the attainable accelerating voltage, a second belt has been installed so that more charge can be sent up. Characteristics of the machine have changed considerably after installing the second belt and tests are under way to obtain the optimum performance. However, it is doubtful if the accelerating voltage can be increased beyond 500 KV. In a bigger, dehumidified room, it may be possible to obtain about a million volts without much difficulty.

It is of interest to note that the effort spent in developing the accelerator amounts to about 8 man-years of work by the scientific staff and 6 man-years of work by the workshop staff. The cost of equipment and materials used in the machine is about Rs. 50,000.

5. ACKNOWLEDGMENTS

We are grateful to Dr. D. Y. Phadke for his continued interest in the development of the accelerator. Our thanks are due to our colleagues, Dr. A. P. Thatte, Mr. S. S. Samant and Mr. T. Singh for helping us in various ways. We wish to thank our Sectional Mechanic, Mr. M. L. Uplekar, for his enthusiastic and skilful work. Mention must be made of the T.I.F.R. Workshop staff and, in particular, Mr. B. S. Naik, for their co-operation and assistance at all stages.

THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF *ORTHO*- AND *META*-THIOCRESOLS

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Abstract

The absorption spectra of *ortho*- and *meta*-thiocresols have been studied in the present investigation. The ortho-thiocresol spectrum consists of about forty-five bands of rather a diffuse nature and in general low intensity in the region from 2873 Å to 2600 Å. The maximum number of bands is obtained by using a path length of 330 cm. for absorption, the temperature of the bulb being maintained at 14° C. Several of these bands are assigned as due to v-v-transitions. The (0, 0) band is chosen at 35386 cm.$^{-1}$ which is the strongest band on the longer wavelength side. Vibrational frequencies in the excited state have values 729, 957 and 1159 and combinations and overtones of these are present.

The *meta*-thiocresol spectrum consists of about forty bands of rather a diffuse nature and very weak intensities in the region from 2900 Å to 2590 Å. The maximum number of bands is obtained by using a path length 200 cm. for absorption and by keeping the temperature of the bulb at 20° C. The (0, 0) band is chosen to be that at 34793 cm.$^{-1}$ which is the strongest band on the longer wavelength side. Vibrational frequencies in the excited state have values 492, 611, 720, 845, 965, 1016 and 1155 cm.$^{-1}$ and combinations and overtones of these are present.

Introduction

Work on the absorption spectra of *ortho*- and *meta*-thiocresols has been reported in the collection of ultraviolet spectral data of the American Petroleum Institute Research Project 44, Serial Nos. 433 and 435. The spectrum of *ortho*-thiocresol in *iso*-octane solution shows one peak at about 2880 Å, the other at 2790 Å and the third at 2340 Å. In case of *meta*-thiocresol studied in *iso*-octane solution there are three peaks at 2890 Å, 2795 Å and at 2385 Å. Different concentrations were used to plot the graph showing the absorption against the wavelength. Work on the absorption spectrum of *para*-thiocresol has been recently reported by the author.[1] So far no

work on the vapour absorption spectra of *ortho*- and *meta*-thiocresols in the ultraviolet region appears to have been reported. The infra-red spectral data and the Raman spectrum data do not appear to have been reported for these molecules. The infra-red and Raman spectral data are being reported elsewhere. The ultraviolet absorption spectra in the vapour state and the effect of changing the temperature of the absorbing column and the length of the column have been studied and reported now. Assignments have been made and discussed.

EXPERIMENTAL

Ortho-thiocresol and *meta*-thiocresols are colourless liquids with boiling points 194·3° C. and 195° C. respectively. These chemicals were supplied by Eastman Kodak Company. The experimental procedure adopted is the same as described in detail in the absorption spectrum of *para*-thiocresol.[1]

RESULTS

Ortho-thiocresol in vapour phase shows strong absorption below 2550 Å. At room temperature 30° C. and an absorption path length of 100 cm. the bands appear in the region 2900 Å to 2600 Å. With increase in temperature of the absorbing column to 50° C. the bands on the shorter wavelength side begin to disappear and when the temperature is raised to 80° C., there is continuous absorption from 2900 Å to the lower wavelength side. No bands develop on the long wavelength side. On increasing the length of the absorbing column to 330 cm. and keeping the temperature of the bulb at 14° C. all the bands mentioned in Table I below were recorded.

Meta-thiocresol in solution phase absorbs in the region 2900 Å to 2600 Å, and there is strong continuous absorption below 2600 Å. In the vapour absorption about forty bands were obtained between 2900 Å to 2590 Å. At room temperature and an absorption path length 100 cm. the bands are present in this region with weak intensities. When the temperature is raised to 50° C. most of the bands on the shorter wavelength side disappear and on raising the temperature to 80° C. there is continuous absorption starting from 2900 Å towards the shorter wavelength side. No new bands appear to develop on the longer wavelength side. On increasing the length of the absorbing column to 200 cm. and evacuating the tube and keeping the bulb at 20° C. all the bands mentioned in Table II were recorded.

The data on the observed bands together with the proposed assignments are given in Tables I and II for *ortho*- and *meta*-thiocresols respectively, and the analysis discussed.

TABLE I

Ortho-*thiocresol bands* 2800 *Å system*

The intensities of the bands were visually estimated and explained as below. *s*, strong; *ms*, medium strong; *m*, medium; *w*, weak; *vw*, very weak.

λ in Å	ν in cm.$^{-1}$	Int. visual estimation	Separation from (0, 0), *i.e.*, 35386 cm.$^{-1}$	Assignment
2872·2	34806	*w*	− 580	
2866·8	34871	*w*	− 515	
2863·8	34908	*vw*	− 482	0−4×120
2857·2	34990	*vw*	− 396	
2854·9	35017	*w*	− 369	0−3×120
2849·9	35079	*w*	− 307	0−2×120−60
2844·4	35146	*w*	− 240	0−233
2841·4	35183	*w*	− 203	0−203
2837·8	35228	*w*	− 158	0−158
2834·7	35266	*w*	− 120	0−120
2830·0	35325	*vw*	− 61	0−61
2825·1	35386	*vs*	0	(0, 0)
2811·1	35562	*w*	176	
2803·0	35665	*w*	279	
2790·9	35820	*w*	434	
2779·4	35968	*w*	582	0+729−158
2773·0	36051	*w*	665	0+729−60
2768·1	36115	*s*	729	0+729
2765·3	36151	*w*	765	0+957−203
2760·7	36212	*w*	826	0+957−120
2755·9	36275	*w*	889	0+957−60
2750·7	36343	*s*	957	0+957
2744·1	36431	*w*	1045	0+1159−120
2739·8	36488	*w*	1102	0+1159−60
2735·5	36545	*s*	1159	0+1159
2729·1	36631	*w*	1245	0+2×729−203
2725·5	36679	*w*	1293	0+2×729−158
2721·3	36736	*w*	1350	0+2×729−120
2713·9	36836	*ms*	1450	0+2×729
2705·7	36948	*w*	1562	0+957+729−120
2700·4	37020	*w*	1634	0+957+729−60
2695·8	37083	*ms*	1697	0+957+729
2692·3	37131	*w*	1745	0+2×957−158
2684·5	37239	*w*	1853	0+2×957−60
2680·5	37295	*ms*	1909	0+2×957
2676·4	37352	*w*	1966	0+957+1159−158
2665·7	37502	*m*	2116	0+957+1159
2655·8	37642	*w*	2256	0+2×1159−60
2651·2	37707	*m*	2321	0+2×1159
2639·2	37878	*vw*	2492	0+2×957+729−158
2636·0	37924	*vw*	2538	0+2×957+729−120
2628·5	38033	*w*	2647	0+2×957+729
2620·5	38149	*w*	2763	0+3×957−120
2612·7	38263	*m*	2877	0+3×957
2604·1	38389	*vw*	3003	0+2×957+1159−60
2599·1	38463	*mw*	3077	0+2×957+1159

TABLE II

Meta-*thiocresol bands* 2900 *Å to* 2590 *Å region*

The intensities of the bands were visually estimated and explained as below. *vs*, very strong; *s*, strong; *ms*, medium strong; *m*, medium; *w*, weak; *mw*, medium weak; *vw*, very weak.

λ in Å	ν in cm.$^{-1}$	Int. visual estimation	Separation from (0, 0) *i.e.*, 34793 cm.$^{-1}$	Assignment
2901·5	34454	*w*	− 339	0−223−121
2892·0	34568	*w*	− 225	0−223*
2888·4	34611	*w*	− 182	0−177*
2885·6	34644	*w*	− 149	0−146*
2883·6	34668	*w*	− 125	0−121*
2881·9	34689	*w*	− 104	
2878·1	34734	*vw*	− 59	
2873·3	34793	*vs*	0	(0, 0)
2855·3	35012	*w*	219	
2846·0	35126	*w*	333	
2838·4	35220	*w*	433	
2833·2	35285	*s*	492	0+492
2827·8	35352	*w*	559	
2823·7	35404	*s*	611	0+611
2815·0	35513	*s*	720	0+720
2805·1	35638	*s*	845	0+845
2795·7	35758	*s*	965	0+965
2790·7	35809	*s*	1016	0+1016
2780·9	25948	*s*	1155	0+1155
2767·5	36123	*m*	1330	0+845+492
2757·1	36259	*m*	1466	0+965+492
2748·2	36376	*m*	1583	0+965+611
2742·6	36450	*m*	1657	0+1155+492
2740·9	36473	*m*	1680	0+965+720
2734·9	36553	*ms*	1760	0+1155+611
2730·9	36607	*ms*	1814	0+965+845
2726·0	36672	*ms*	1879	0+1155+720
2722·6	36718	*ms*	1925	0+965+965
2714·5	36828	*ms*	2035	0+2×1016
2709·0	36903	*ms*	2110	0+965+1155
2705·0	36957	*ms*	2164	0+1016+1155
2694·7	37098	*ms*	2305	0+2×1155
2669·3	37451	*ms*	2658	0+2×965+720
2660·7	37572	*w*	2779	0+2×965+845
2653·1	37680	*m*	2887	0+3×965
2647·3	37763	*w*	2970	0+845+965+1155
2642·4	37833	*w*	3040	0+3×1016
2639·7	37871	*w*	3078	0+2×965+1155
2613·5	38251	*w*	3458	0+3×1155
2603·0	38405	*w*	3612	0+3×965+720
2593·7	38543	*w*	3750	0+3×965+845

* Observed in Raman spectrum.

Discussion and Analysis

Ortho-*thiocresol*

The strong band on the longer wavelength side at 2825 Å is taken as the (0, 0) band. The other strong bands at 2768 Å, 2750 Å and 2735 Å are separated from the (0, 0) band by 729, 957 and 1159 cm.$^{-1}$ respectively. Combinations and overtones of these frequencies are present as shown in the analysis. The excited state frequency 729 giving the strong band at 2768 Å is correlated with the medium strong Raman frequency of 795 cm.$^{-1}$ and the medium strong infra-red frequency 797 cm.$^{-1}$ The frequency near about 957 cm.$^{-1}$ is a frequency which is observed to be present in practically all the *ortho*-disubstituted molecules as shown in Table III. This frequency is correlated with the very strong Raman frequency 1047 cm.$^{-1}$ and the corresponding strong infra-red frequency 1046 cm.$^{-1}$. The spectrum of *ortho*-thiocresol is similar to that of *ortho*-cresol[5, 6] and *ortho*-xylene.[3] The excited state frequency 957 cm.$^{-1}$ in *ortho*-thiocresol, 944 cm.$^{-1}$ in *ortho*-cresol, 939 cm.$^{-1}$ in *ortho*-xylene, 957 cm.$^{-1}$ in *ortho*-dichloro-benzene[8] perhaps involve similar modes of vibration. The third progression forming frequency is 1159 cm.$^{-1}$ This frequency is correlated with the medium strong Raman frequency 1209 cm.$^{-1}$ and the medium strong infra-red frequency 1217 cm.$^{-1}$ This may be tentatively assigned to the C—CH_3 stretching vibration. In addition to these fundamental vibration frequencies, there are bands separated by 60, 120, 158 and 203 cm.$^{-1}$ respectively from the progression forming frequencies. These bands may be assigned as due to v-v transitions. On comparing the shift of the (0, 0) band in the case of *ortho*-disubstituted molecules studied so far it is found that it is the largest in *ortho*-thiocresol.

Meta-*thiocresol*

It is observed that the *meta*-thiocresol bands are in general very diffuse. This has also been observed in case of the *meta*-cresol[5] and *meta*-xylene bands.[3] Sponer and Cooper put down the causes of diffuseness as (i) due to overlapping transitions, (ii) due to overlapping of the gross and fine structure of bands, and (iii) due to internal rotation of the CH_3 group. The first two of these are in general applicable to other substituted benzene molecules also. In case of *meta*-thiocresol the bands are very diffuse and the v-v transitions are overlapping to such an extent that it was difficult to measure the wavelengths of the bands due to v-v-transitions on account of the very low intensity of all the bands in the spectrum and specially extremely low intensity of the bands due to v-v-transitions. As such the analysis for the prominent bands only is given in Table II.

The band at 34793 cm.$^{-1}$, the strongest band in the absorption spectrum on the longer wavelength side, is taken as the (0, 0) band. The frequencies 492, 611, 720, 845, 965, 1016 and 1155 involved in the strong bands at 35285, 35404, 35513, 35638, 35758, 35809 and 35948 cm.$^{-1}$ are taken as fundamental vibrational frequencies of the molecule in the electronically excited state in the analysis of the absorption spectrum of *meta*-thiocresol.

The frequency 492 cm.$^{-1}$ may be correlated with the frequency 523 cm.$^{-1}$ with medium intensity in the Raman spectrum. The frequency 611 cm.$^{-1}$ can be correlated with the medium strong intensity frequency 685 cm.$^{-1}$ observed in the Raman effect and the strong frequency 686 cm.$^{-1}$ observed in the infra-red spectrum. The frequency 720 cm.$^{-1}$ is correlated with the very strong frequency 772 cm.$^{-1}$ observed in the infra-red spectrum. The frequency 845 cm.$^{-1}$ is correlated with the strong frequency 853 cm.$^{-1}$ in the infra-red and 855 cm.$^{-1}$ in the Raman spectrum.

The excited state frequency 965 cm.$^{-1}$ is correlated with the very strong Raman ground state frequency 1001 and 982 cm.$^{-1}$ in the infra-red. This frequency appears in combination with all the other excited state frequencies. This frequency appears in the excited state in case of *meta*-fluoro-toluene,[2] *meta*-cresol,[5] *meta*-xylene,[3] *meta*-fluoro-chloro-benzene,[4] and *meta*-dichlorobenzene[8] as shown in Table IV, and involves similar mode of vibration. This seems to be the characteristic excited state frequency present in all the *meta*-disubstituted benzenes.

The 1016 cm.$^{-1}$ excited state frequency may possibly be correlated with the Raman frequency 1084 cm.$^{-1}$ appearing with medium intensity and with 1083 cm.$^{-1}$ appearing with medium strong intensity in the infra-red spectrum. A similar frequency 1031 cm.$^{-1}$ in the excited state with the corresponding Raman line at 1086 cm.$^{-1}$ is observed in case of *meta*-cresol also.[5]

The frequency 1155 cm.$^{-1}$ may be correlated with 1218 cm.$^{-1}$ having medium intensity in the infra-red and 1222 cm.$^{-1}$ with medium strong intensity in the Raman spectrum. This is assigned to C—CH_3 stretching vibration. It is also observed that the shift of the (0, 0) band towards longer wavelength from the (0, 0) band of benzene is in the case of *meta*-thiocresol the largest of all meta-disubstituted benzenes.

It is also observed that the (0, 0) band shifts to the longer wavelength side as we go from *ortho*- to *meta*- and to *para*-thiocresol. The (0, 0) band in *ortho*-, *meta*- and *para*-thiocresols being at 35386 cm.$^{-1}$, 34793 cm.$^{-1}$ and 34222 cm.$^{-1}$ respectively. It has also been observed by Cave and Thompson that along the series *o*-, *m*-, *p*- for cresols or fluoro-toluenes the position of the (0, 0) transition moves towards lower frequencies.[2]

Table showing the comparison of the excited state frequencies in ortho-disubstituted benzenes

O-Dichloro-benzene[10]	O-Dichloro-benzene[8]	O-Fluoro-chloro-benzene[4]	O-Xylene[2]	O-Cresol[5]	O-Chloro-toluene[9]	O-Fluoro-toluene[3]	O-Thio-cresol	
36232	36230	37035	37308	36418	36838	37576	35386	(0, 0) band in cm.$^{-1}$
307	944 (1041 R)	477	507	124	368	707	729	
437	957 (1020 R)	513	692	202	460	924	957	
610	1089 (1129 R)	639	939	360	530	1230	1159	
958		794 (830 R)	1195	702	625			
1089		929 (1031 R)		719	680			
1486		1076 (1127 R)		944	813			
		1248 (1237 R)		955	915			
				1251	1005			
					1084			
					1192			
vv	*vv*	*vv*	*vv*	*vv*			*vv*	
24	25 cm.$^{-1}$	99 cm.$^{-1}$	56	63			60	
59	60 cm.$^{-1}$	274 cm.$^{-1}$	60	73			120	
			72	97			158	
			76	115			203	
			126					

TABLE IV

Table showing comparison of excited state frequencies of meta-*disubstituted benzenes*

M-Dichloro-benzene[8]	M-Fluoro-chloro-benzene[4]	M-Xylene[3]	M-Cresol[5]	M-Chloro-toluene[9]	M-Fluoro-toluene[2]	M-Thio-cresol	
36186	37027	36955	35985	36619	37398	34793	(0, 0) band in cm.$^{-1}$
960 (1000 R)	160 (245)	470	116	418	282	492	
	325 (410)	675	188	476	457	611	
1089 (1070 R)	455 (519)	735	251	612	684	720	
	636 (683)	965	469	711	965	845	
1103 (1126)	846 (883)	1145	696	778	1261	965	
	966 (1003)	1250	964	851		1016	
	1023 (1063)		1031	981		1155	
	1218 (1221)			1211			
vv 63			*vv* 47				
70			82				
147 cm.$^{-1}$			126				
			200				

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It is further observed that the intensities in the case of *ortho-*, *meta-* and *para*-thiocresols are in agreement with the observation by Sklar[7] the ratios of these being approximately as 1 : 1 : 4.

The absorption spectra in case of thiocresols are in general of very low intensity as compared to those of cresols. This may be due to the effect of the substitution of the SH group in place of OH in cresols.

Summary

The spectra of the *ortho-*, *meta-*, and *para*-thiocresols are similar to those of the respective cresols. Excited state frequencies in *ortho-* and *meta*-thiocresols have been discussed. The frequency near 1210 cm.$^{-1}$ is assigned to C—CH_3 stretching vibration. In thiocresols SH is substituted in place of OH in cresols. This substitution of SH in place of OH causes the (0, 0) band to shift to the longer wavelength side as compared to the (0, 0) band in respective cresols and of all the disubstituted benzenes the (0, 0) band in case of *ortho-*, *meta-* and *para*-thiocresols is to the longest wavelength side.

Substitution of SH in place of OH has also a marked effect on the intensity of the bands in the spectra. This intensity in case of thiocresol bands is very much low as compared to the intensity in case of the respective cresols.

Acknowledgement

The author is indebted to Professor R. K. Asundi and Dr. M. R. Padhye for their keen interest in this work.

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FORMYLATION OF POLYHYDROXY FLAVONES AND CHROMONES

By V. V. S. Murti, T. R. Seshadri, F.A.Sc., V. Sundaresan and B. Venkataramani

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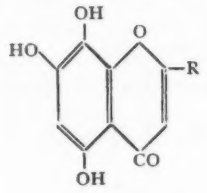
Abstract

In the case of nor-wogonin and 5:7:8-trihydroxy-2-methyl-chromone, Gattermann method is efficient in yielding the corresponding aldehydes, whereas with their 8-methyl ethers hexamine method works satisfactorily.

In connection with the synthesis of furano compounds, the preparation of hydroxy aldehydes of flavones and chromones was important. The hexamine method (Duff's method) has been used successfully in a number of cases. With more complex types especially with a larger number of free hydroxyls present in the molecule, it does not work well. For instance, the trihydroxy compounds, nor-wogonin (I *a*) and 5:7:8-trihydroxy-2-methyl chromone (I *b*) yield only coloured products containing nitrogen and no aldehyde could be obtained. Hence other methods have been investigated; as an alternative the simpler Gattermann reaction using zinc cyanide works very successfully to yield the 6-aldehydes (II *a*, II *b*).



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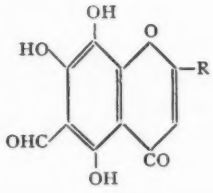
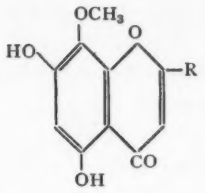


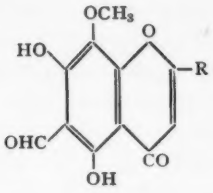
II

(*a*) R=C_6H_5
(*b*) R=CH_3

As examples of 5:7-dihydroxy compounds with the 8-position substituted by a methoxyl group, wogonin (III *a*) and 8-methoxy-5:7-dihydroxy-2-methyl chromone (III *b*) have now been examined and the hexamine method is found to give satisfactory yields of 6-aldehydes (IV *a*, IV *b*).



III



IV

(*a*) R=C_6H_5
(*b*) R=CH_3

5:7:8-Trihydroxy-2-methyl chromone-6-aldehyde (II *b*) has also been prepared in good yield in an independent way starting with visnagin which was degraded to 5:7-dihydroxy-2-methyl chromone 6-aldehyde according to the method of Schönberg *et al.*,[1] and subjected to oxidation with alkaline persulphate.

Experimental

Nor-wogonin-6-aldehyde (*II a*).—A suspension of nor-wogonin (I *a*) (1·5 g.) in anhydrous ether (200 c.c.) was treated with zinc cyanide (6 g.) and aluminium chloride (5 g.) and the mixture saturated with hydrogen chloride while cooling in ice. In half an hour, a heavy dark liquid separated and the supernatant ether assumed a red colour. The gas was passed for 6 hr. more and the mixture left in the ice-bath overnight. After decanting off the ether layer, the residue was washed with ether and heated with water (100 c.c.) in a boiling water-bath for 20 min. The yellow product that separated was a mixture of nor-wogonin and its 6-aldehyde; the two could be separated by fractional crystallisation from alcohol-acetone mixture in which the aldehyde was less soluble and hence was left behind. From the mother liquor unchanged nor-wogonin (0·5 g.) was isolated. The aldehyde crystallised from alcohol-acetone mixture as golden yellow prismatic needles (0·6 g.), m.p. 270–72° (d.). Mixed m.p. with nor-wogonin (m.p. 254°) was 230° (d.) (Found: C, 64·0; H, 3·1; $C_{16}H_{10}O_6$ requires C, 64·4; H, 3·4%). It gave a green colour with ferric chloride becoming dark with excess of the reagent. The dinitrophenyl hydrazone crystallised as lemon yellow tiny prisms, m.p. 345° (d.).

5:7:8-*Trihydroxy-2-methyl-chromone-6-aldehyde* (*II b*).—(i) 5:7-Dihydroxy-2-methyl chromone-6-aldehyde[1] (1·2 g.) was mixed with potassium hydroxide solution (1·2 g. in 50 c.c. of water) and the resulting mixture treated dropwise with aqueous solution of potassium persulphate (2·4 g. in 100 c.c. of water) during 6 hr. and set aside overnight. It was acidified with hydrochloric acid and the unchanged chromone aldehyde (0·5 g.) extracted

with ether. The aqueous solution was heated with more of acid and sodium sulphite at 100°. The product was extracted with chloroform; after evaporating the solvent, the residue was extracted with ether and the ether-soluble portion finally crystallised from methanol-benzene mixture yielding yellow rectangular plates and prisms (0·2 g.) turning brown at 245° and decomposing at 258–60° (Found: C, 56·2; H, 3·6; $C_{11}H_8O_6$ requires C, 55·9; H, 3·4%). The dinitrophenyl hydrazone was obtained as orange yellow small prisms which darkened at 330° and did not melt up to 360°.

(ii) 5:7:8-Trimethoxy-2-methyl chromone[2] was subjected to demethylation using aluminium chloride and benzene.[3] 5:7:8-Trihydroxy-2-methyl chromone crystallised from dilute methanol as yellow rhombic prisms, m.p. 236–38° (Found: C, 57·9; H, 3·8; $C_{10}H_8O_5$ requires C, 57·7; H, 3·9%). With alcoholic ferric chloride it gave a deep green colour changing to brown with excess of the reagent. With aqueous sodium hydroxide it gave a yellow solution which turned purple on shaking with air and then faded. Remethylation with excess of dimethyl sulphate and anhydrous potassium carbonate in acetone solution yielded the original trimethyl ether. The trihydroxy-2-methyl chromone (1·2 g.) was subjected to Gattermann's reaction using zinc cyanide (5 g.) and aluminium chloride (5 g.). The product was worked up as usual and it crystallised from methanol-benzene mixture as rectangular plates and prisms (0·1 g.), m.p. 260–61° (d.) alone or when mixed with the sample obtained by method (i). The mother liquor yielded unchanged original chromone (0·4 g.).

Wogonin-6-aldehyde (*IV a*).—The required 5:8-dimethoxy-7-hydroxy flavone was prepared by the method of Sastri and Seshadri[4] except that pyridine-potash procedure was employed for the conversion of the acetophenone into the diketone. Subsequent partial demethylation was carried out according to Shah *et al.*[5]; it was necessary to use more nitrobenzene in order to get improved yields of wogonin (III *a*).

The aldehyde was obtained by heating a mixture of wogonin (0·35 g.), hexamine (2 g.) and glacial acetic acid (20 c.c.) at 100° for 6 hr. A mixture of concentrated hydrochloric acid and water (1:1, 20 c.c.) was then added and the heating continued for 15 min. more, during which period an yellow crystalline solid separated. The mixture was diluted with water and kept in the refrigerator. The aldehyde that separated was crystallised from benzene or acetic acid yielding pale yellow prismatic needles (0·2 g.), m.p. 257–58° (Found: C, 65·2; H, 4·2; $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%). It gave a pink brown colour with alcoholic ferric chloride. The dinitrophenyl hydrazone formed aggregates of orange red tiny prisms, m.p. 290–92° (d.).

8-Methoxy-5: 7-dihydroxy-2-methyl chromone (*III b*).—The intermediate 2-hydroxy-3: 6-dimethoxy-4-benzyloxy-ω-acetyl acetophenone was earlier prepared by Geissman[6] but was not characterised. The C-acylation of the corresponding acetophenone has now been carried out in the usual manner using sodium and ethyl acetate; the diketone crystallised from benzene-petroleum ether as stout prisms, m.p. 102–03° (Found: C, 66·2; H, 6·2; $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·8%). It gave a violet-brown colour with ferric chloride which changed to deep violet on standing. The debenzylation of 5: 8-dimethoxy-7-benzyloxy-2-methyl chromone was carried out by Geissman by catalytic hydrogenation. In the present work it has been done using a mixture of acetic acid and hydrochloric acid.

5: 8-Dimethoxy-7-hydroxy-2-methyl chromone (0·5 g.) was dissolved in dry dioxane (75 c.c.) and allowed to cool. Aluminium chloride (1 g. dissolved in 100 c.c. of dioxane) was added and mixture allowed to stand at room temperature for 48 hr. The complex was decomposed by means of concentrated hydrochloric acid and the mixture extracted with chloroform, and the solvent distilled under diminished pressure. The residue was purified by dissolving in ether which left behind some impurity and finally it crystallised from benzene as colourless aggregates of prisms (0·2 g.), m.p. 190–92° (Found: C, 59·3; H, 4·7; $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%). The chromone dissolved in aqueous sodium carbonate and sodium hydroxide giving yellow solutions. With alcoholic ferric chloride, it gave a violet colour which turned green with more of the reagent.

8-Methoxy-5: 7-dihydroxy-2-methyl chromone-6-aldehyde (*IV b*).—A mixture of the foregoing chromone (0·7 g.), hexamine (3 g.) and glacial acetic acid (30 c.c.) was heated in a boiling water-bath for 6 hr. The mixture was worked up as in an earlier case and the aldehyde separated from alcohol as yellow rectangular tablets (0·5 g.), m.p. 188–89 ° (Found: C, 57·2; H, 3·9; $C_{12}H_{10}O_6$ requires C, 57·6; H, 4·0%). It gave a pink-violet colour with alcoholic ferric chloride. The dinitrophenyl hydrazone was obtained as orange yellow needles, m.p. 290–92° (d.).

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REDUCTION OF SOLVABLE GROUPS

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Monomial Representations

Representations of solvable groups can be elegantly studied with the help of monomial representations. Let G be a group of finite order and U be a subgroup of G. Let

$$G = \sum_{r=1}^{k} g_r U$$

be a left coset decomposition of G with respect to U. In this decomposition the choice of the elements g_r is not unique but when they are chosen once, they are taken as fixed for the subsequent discussion. Every element g of G could be written as $g_r u$, where u belongs to U. Consider the product $gg_i = g_r u g_i$. This element could be written as the product of some g_j and u' uniquely, where u' belongs to U. Now construct the matrix whose i-th row j-th column element is u' and all the other elements in the i-th row are zeros. It is easily verified that these matrices define a representation of the group G. More general representations[1] of G could be defined with respect to U and a normal subgroup H of U. These are called the monomial representations of G. We are, however, making use of only representations in which H is always taken as consisting of the identity element only. The monomial representations of G that could be obtained either by taking different sets of elements g_r in the coset decomposition or by taking different subgroups U[1] conjugate to U are all equivalent.

Representations of G when G/U is of Prime Order

Let U be a normal subgroup of G and let G/U be a cyclic group of prime order say r. Then G may be written in the form $G = \sum_{k=0}^{r-1} s^k U$, where s is some element in G not contained in U. Let $R^{(0)}$ be an irreducible representation of U and let the matrix corresponding to an element u of U be $R_u{}^{(0)}$. From the representation $R^{(0)}$, we obtain the representations $R^{(i)}$ $\{i = 1, 2, \ldots, (r-1)\}$ of U by making u to correspond to the matrix $R_u{}^{(i)} = R_{s^{-i}us^i}$. If in the monomial representation of G defined with

respect to U, the elements of U are replaced by the corresponding matrices in the representation $R^{(0)}$ of U, we obtain a matrix representation R of G and we have the following two theorems given by Seitz.[2]

Theorem 1.—The representations $R^{(i)}$ of U, for different values of i, are all either non-equivalent or equivalent.

Theorem 2.—If all the representations are non-equivalent, R is an irreducible representation of G and if they are all equivalent, R is reducible into r non-equivalent irreducible representations.

Definition.—We define the set of representations $R^{(i)}$ when they are non-equivalent as forming a degenerate star with r arms. When they are equivalent, they may be taken as identical with one of them say $R^{(0)}$ and $R^{(0)}$ itself defines a (non-degenerate) star. A set of irreducible representations of U with one member from each star is defined as a basis set of representations of U with respect to G.

Theorem 3.—The irreducible representations of G which are obtained from a basis set of representations of U, form a complete set of irreducible representations of G.

Proof.—Let U possess a_k, k-dimensional ($k = 1, 2, \ldots, s$) irreducible representations forming a complete set. Then we have the orthogonality relation $\sum_{k=1}^{s} a_k k^2 = N(U)$, the order of the group U. Among these representations of U let b_1 one dimensional representations, b_2 two dimensional representations, etc., be the total number of representations belonging to degenerate stars and let the others belong to the non-degenerate stars. Every degenerate star is of order r. Then from Theorem 2, it follows that G contains $r\ (a_1 - b_1)$ one dimensional, $r\,(a_2 - b_2)$ two dimensional, etc., irreducible representations arising from the non-degenerate star and b_1/r, r-dimensional, b_2/r, $2r$-dimensional, etc., irreducible representations arising from the degenerate stars. All these representations are non-equivalent as they correspond to different stars. Now the relation

$$\sum_{k=1}^{s} r\,(a_k - b_k)\,k^2 + \frac{b_k}{r} \cdot r^2 = r \sum_{k=1}^{s} a_k \cdot k^2 = r\,N(U),$$

shows that all the representations of G are obtained in the above enumeration.

Solvable Groups

Let G be a solvable group and B a normal Abelian subgroup (preferably largest) of G. The irreducible representations of the Abelian group B are

all one dimensional and there are as many non-equivalent irreducible representations of B as there are elements in it. Let $b_p^{(r)}$ be the complex number in the r-th irreducible representation corresponding to the element p of B. Now every element s of G defines a mapping sBs^{-1} of B on to itself. Every such mapping transforms the representation $b^{(r)}$ into a representation in which the element sps^{-1} corresponds to the number $b_p^{(r)}$. The latter representation may be the same as the representation $b^{(r)}$ or may be distinct from it. All the elements of G which transform the representation $b^{(r)}$ into itself form a group $G^{(r)}$ containing B. All the elements of G which transform the representations $b^{(r)}$, $b^{(s)}$, etc., simultaneously into themselves form a group which is the intersection of the groups $G^{(r)}$, $G^{(s)}$, etc. Elements of G belonging to the same coset $s_iG^{(r)}$ transform the representation $b^{(r)}$ into identical representations of B and elements belonging to two different cosets $s_iG^{(r)}$ and $s_jG^{(r)}$ transform $b^{(r)}$ into distinct representations of B. As before, we call the set of all distinct irreducible representations of B which are conjugate with respect to each other in relation to the elements of G, a star and each member an arm of the star. If we select one representation from each star we obtain a basis set of irreducible representations of B defined with respect to G. The groups $G^{(r)}$, $G^{(s)}$, etc., which correspond to different irreducible representations of B in the same star are conjugate subgroups of G.

NON-SPURIOUS REPRESENTATIONS OF $G^{(r)}$

$G^{(r)}$ is a solvable group, as it is a subgroup of the solvable group G. The irreducible representations of $G^{(r)}$ could be obtained from those of B using Theorem 2 by stages. However, it is not necessary to obtain all the irreducible representations of $G^{(r)}$, for complete reduction of G. By the method of Theorem 2, it is sufficient to obtain those representations of $G^{(r)}$ which could be generated from the representation $b^{(r)}$ of B with respect to which the group $G^{(r)}$ itself is defined. These representations are called non-spurious representations. The representations of $G^{(r)}$ which arise from those of B other than $b^{(r)}$ may be called spurious representations. Suppose

$$G^{(r)} = G_0^{(r)} \supset G_1^{(r)} \supset \ldots \supset B$$

be a composition series of $G^{(r)}$ containing the group B. Using the argument of Theorem 3 the following result may easily be proved.

Theorem 4.—If there are a_k, k-dimensional non-spurious representations of $G_t^{(r)}$ that could be obtained from the representation $b^{(r)}$ of B

$$\Sigma a_k \cdot k^2 = \frac{N(G_t^{(r)})}{N(B)}$$

where the summation extends over all the non-spurious representations of $G_t^{(r)}$.

It may be noted that in all these non-spurious representations of $G_t^{(r)}$, for every t in the composition series, the matrix corresponding to an element p of B is a scalar matrix with the scalar multiple $b_p^{(r)}$.

Suppose $b^{(s)}$ and $b^{(t)}$ be two different irreducible representations of B, then we have the following theorem.

Theorem 5.—The irreducible representations of $A = G^{(s)} \cap G^{(t)}$ induced by the non-spurious representations of $G^{(s)}$ are distinct from those induced by $G^{(t)}$ when $s \neq t$.

Proof.—The Abelian group B is a subgroup of A and in the representations induced by the non-spurious representations of $G^{(s)}$ and $G^{(t)}$, scalar matrices with different scalar multiples $b_p^{(s)}$ and $b_p^{(t)}$ correspond to an element p of B respectively. Thus the representations of A are non-equivalent. Let $M^{(s)}$ and $M^{(t)}$ be two non-spurious representations of $G^{(s)}$ and $G^{(t)}$ respectively. From the above theorem we have

$$\Sigma\ (tr M_a^{(s)})\ (tr^* M_a^{(t)}) = 0 \tag{7}$$

the summation extending over all elements of A.

Representations of G

Let a left coset decomposition of G with respect to $G^{(r)}$ be given by

$$G = \sum_{i=1}^{r} s_i G^{(r)}.$$

In the monomial representation of G using the above coset decomposition, the matrix corresponding to $s_t g^{(r)}$ contains in the i-th row, i-th column (*i.e.*, the i-th diagonal element) an element $g'^{(r)}$ provided that

$$s_t g^{(r)} s_i = s_i g'^{(r)}.$$

Then $s_t g^{(r)}$ belongs to the group $s_i G^{(r)} s_i^{-1}$, which is conjugate to $G^{(r)}$. Conversely, every element g of G belonging to the group $s_i G^{(r)} s_i^{-1}$, is of the form $s_i g^{(r)} s_i^{-1}$, and will have in the monomial representation of G with respect to $G^{(r)}$, the element $g^{(r)}$ as the i-th diagonal element. In the monomial representation the matrix corresponding to g will have as many diagonal elements as there are subgroups $s_t G^{(r)} s_t^{-1}$ which contain the element g.

Theorem 6.—The matrix representation R of G, obtained from a monomial representation of G with respect to $G^{(r)}$ making use of a non-spurious representation of $G^{(r)}$, is an irreducible representation of G.

Proof.—Let $M^{(\tau_1)}$ be a non-spurious representation of $G^{(\tau_1)} = G^{(\tau)}$ and $M^{(\tau_i)}$ that of $s_i G^{(\tau)} s_i^{-1} = G^{(\tau_i)}$ which is obtained from the non-spurious representation of $G^{(\tau_1)}$ by the transformation of $M^{(\tau_1)}$ by s_i. Let $tr\ M_g^{(\tau_i)}$ be the trace of the element g in the representation $M^{(\tau_i)}$ if g belongs to the group $G^{(\tau_i)}$ and zero otherwise. Then

$$tr R_g = \sum_{i=1}^{k} tr M_g^{(\tau_i)}. \tag{8}$$

Now,

$$\begin{aligned}
\sum_g (tr R_g)(tr^* R_g) &= \sum_g \left(\sum_{i=1}^{k} tr M_g^{(\tau_i)} \right) \left(\sum_{i=1}^{k} tr^* M_g^{(\tau_j)} \right) \text{ from (8)} \\
&= \sum_g \sum_{i,j} (tr M_g^{(\tau_i)})(tr^* M_g^{(\tau_j)}) \\
&= \sum_{i,j} \sum_g (tr M_g^{(\tau_i)})(tr^* M_g^{(\tau_j)}) \\
&= \sum_i N(G^{(\tau_i)}) \quad \text{by Theorems 4 and 5} \\
&= N(G).
\end{aligned}$$

This shows that the representation R of G is irreducible.

Theorem 7.—Two representations of G which are obtained from two different non-spurious representations $M^{(\tau)}$ and $M'^{(\tau)}$ of $G^{(\tau)}$ are non-equivalent.

Proof.—As in the previous theorem this follows from the fact

$$\sum_g (tr R_g)(tr^* R_g') = 0.$$

Similarly, by making use of Theorem 9 we can prove that two representations of G which are obtained from the non-spurious representations of the groups $G^{(\tau)}$ and $G^{(s)}$ corresponding to two different representations $b^{(\tau)}$ and $b^{(s)}$ in a basis set of representations of U with respect to G, are orthogonal. Finally, we arrive at the following theorem.

Theorem 8.—The representations of G, which are obtained from the non-spurious representations of all the subgroups $G^{(\tau)}$ corresponding to all representations $b^{(\tau)}$ in a basis set of representations of B defined with respect to G, form a complete set.

Proof.—B is an Abelian group and all its irreducible representations are one dimensional. They have been classified into different stars using the elements of G. A basis set of representations $b^{(\tau)}$, $b^{(s)}$, etc., is obtained

by taking one representation from each star. If the degeneracy of the star containing $b^{(r)}$ is d_r, we have

$$\sum_r d_r = \mathrm{N}(\mathrm{B}). \tag{8 a}$$

The number of cosets of $\mathrm{G}^{(r)}$ in G is equal to d_r and we have also the relation

$$d_r \times \mathrm{N}(\mathrm{G}^{(r)}) = \mathrm{N}(\mathrm{G}). \tag{9}$$

The dimension of a matrix representation of G, obtained from the monomial representation of G with respect to $\mathrm{G}^{(r)}$, using for the elements of $\mathrm{G}^{(r)}$ their corresponding matrices in a non-spurious representation of dimension n will be nd_r. Hence, if there are $a_s^{(r)}$, s-dimensional non-spurious representations of $\mathrm{G}^{(r)}$, they give rise to sd_r-dimensional representations of G ($s = 1, 2, 3$, etc.). Therefore we have

$$\sum_s a_s^{(r)} (sd_r)^2 = \frac{d_r^2 \mathrm{N}(\mathrm{G}^{(r)})}{\mathrm{N}(\mathrm{B})} \qquad \text{by Theorem 4.}$$

Now summing over r we have

$$\frac{\sum_r d_r^2 \mathrm{N}(\mathrm{G}^{(r)})}{\mathrm{N}(\mathrm{B})} = \frac{\sum_r d_r \{d_r \mathrm{N}(\mathrm{G}^{(r)})\}}{\mathrm{N}(\mathrm{B})}$$

$$= \frac{\mathrm{N}(\mathrm{G}) \left(\sum_r d_r \right)}{\mathrm{N}(\mathrm{B})} \qquad \text{from (9)}$$

$$= \mathrm{N}(\mathrm{G}). \qquad \text{from (8)}$$

Hence the theorem.

Summary

In this paper a method of obtaining the representations of solvable groups, making use of the non-spurious representations defined with respect to the representations of a normal Abelian subgroup is given and the completeness of these representations is established.

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SOLUTION OF THE DIRAC EQUATION FOR ELECTROMAGNETIC POTENTIALS

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ABSTRACT

Following a work Eliezer (1958), we have solved the Dirac electron equation for electromagnetic potentials. Explicit symmetrical expressions are obtained for the potentials in terms of the electron wave function, its derivatives and a lieanr combination of the potentials.

The Dirac equation,*

$$i\gamma^{\mu}\left(\frac{\partial}{\partial x^{\mu}}+iA_{\mu}\right)\psi+m\psi=0, \tag{1}$$

is usually solved for the electron wave function, ψ, in terms of the electromagnetic potentials, A^{μ}. Eliezer (1958) has recently suggested that it is also of interest to solve the converse problem, namely, to determine the potentials, A^{μ}, in terms of ψ and its derivatives. He has shown that the four equations that one gets from (1) are not all independent. They satisfy a consistency condition,

$$\psi' J\psi = 0 \tag{2}$$

where prime denotes the transpose matrix and

$$J=\begin{pmatrix} 0 & -\partial_t & -(\partial_x+i\partial_y) & -\partial_z \\ \partial_t & 0 & \partial_z & (\partial_x-i\partial_y) \\ (\partial_x+i\partial_y) & -\partial_z & 0 & \partial_t \\ -\partial_z & -(\partial_x-i\partial_y) & -\partial_t & 0 \end{pmatrix} \tag{3}$$

with

$$(\partial_t, \partial_x, \partial_y, \partial_z)=\left(\frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right).$$

* We put $\hbar = 1$, $c = 1$, $e = 1$. Summation in (1) is understood over the suffix μ.

Dirac has given some general arguments to show that J should have the form

$$J = \beta a_x a_z (\partial_t + \alpha_x \partial_x + \alpha_y \partial_y + \alpha_z \partial_z) \tag{4}$$

where

$$\beta = \gamma^0, (\alpha_x, \alpha_y, \alpha_z) = \beta (\gamma^1, \gamma^2, \gamma^3),$$

which is in agreement with (3).

Taking Dirac's representation of the $\vec{\alpha}$ and β matrices, the equation (1) can be written as

$$\begin{aligned}
&- A_0\psi_1 + A_x\psi_4 - iA_y\psi_4 + A_z\psi_3 + b_1 = 0 \\
&- A_0\psi_2 + A_x\psi_3 + iA_y\psi_3 - A_z\psi_4 + b_2 = 0 \\
&- A_0\psi_3 + A_x\psi_2 - iA_y\psi_2 + A_z\psi_1 + b_3 = 0 \\
&- A_0\psi_4 + A_x\psi_1 + iA_y\psi_1 - A_z\psi_2 + b_4 = 0
\end{aligned} \tag{5}$$

where

$$\begin{aligned}
b_1 &= (i\partial_t + m)\psi_1 + i\partial_z\psi_3 + (i\partial_x + \partial_y)\psi_4 \\
b_2 &= (i\partial_t + m)\psi_2 + (i\partial_x - \partial_y)\psi_3 - i\partial_z\psi_4 \\
b_3 &= i\partial_z\psi_1 + (i\partial_x + \partial_y)\psi_2 + (i\partial_t - m)\psi_3 \\
b_4 &= (i\partial_x - \partial_y)\psi_1 - i\partial_z\psi_2 + (i\partial_t - m)\psi_4, \\
(A^0, A^1, A^2, A^3) &= (A_0, -A_1, -A_2, -A_3) \\
&= (A_0, A_x, A_y, A_z),
\end{aligned}$$

and

$$(x^0, x^1, x^2, x^3) = (t, x, y, z).$$

Since only three of these equations are independent, we can solve for any three of the four variables, A_0, A_x, A_y, A_z, in terms of the fourth. Eliezer has given explicit expressions for A_x, A_y, A_z in terms of A_0. This, however, destroys the symmetry among the four potentials. To preserve this symmetry, we introduce a linear combination of these potentials,

$$\begin{aligned}
P &= c_0A_0 + c_1A_x + c_2A_y + c_3A_z \\
&= \sum_{\alpha=1}^{3} c_\alpha A^\alpha
\end{aligned} \tag{6}$$

and solve for A_0, A_x, A_y, A_z in terms of P. We can get Eliezer's result† by choosing the constants c_α as

$$(c_0, c_1, c_2, c_3) = (1, 0, 0, 0).$$

The calculations are rather long though straightforward. Therefore we give only the results here:—

$$A^\mu = \frac{\phi\gamma^\mu [P - (m - i\gamma^\mu\partial_\mu)\Gamma^\mu - iD^\mu]\psi}{\phi S\psi} \tag{7}$$

[$\mu = 0, 1, 2, 3$; no summation over μ here]

where

$$\phi = \psi'\gamma^2\gamma^0 \tag{8 a}$$

$$\partial_\mu = \frac{\partial}{\partial x^\mu} \tag{8 b}$$

$$\Gamma^\mu = \sum_{\alpha\neq\mu} c_\alpha\gamma^\alpha, \qquad \alpha = 0, 1, 2, 3 \tag{8 c}$$

$$D^\mu = \sum_{\alpha\neq\mu} c_\alpha \frac{\partial}{\partial x_\alpha}, \qquad x_\alpha = \sum_{\beta=0}^{3} g_{\alpha\beta}x\beta \tag{8 d}$$

$$S = \sum_{\alpha=0}^{3} c_\alpha\gamma^\alpha \tag{8 e}$$

and we use the metric $g_{00} = 1$, $g_{11} = g_{22} = g_{33} = -1$, $g_{\mu\nu} = 0$, $\mu \neq \nu$.

One can get to Eliezer's notation by replacing‡ A_0 by

$$-\phi, \ (A_x, A_y, A_z) \text{ by } (A_1, A_2, A_3)$$

and

$$\left(\frac{\partial}{\partial x^1}, \frac{\partial}{\partial x^2}, \frac{\partial}{\partial x^3}\right)$$

by

$$(-\nabla_x, -\nabla_y, -\nabla_z).$$

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† Eliezer's equations (25) and (26) are incorrect. They should, respectively, be

$$R = \alpha_y\beta [m\beta + (\phi + i\nabla_t) - \vec{\alpha}\cdot\vec{\nabla}]$$
$$a = \alpha_y\beta.$$

Here Eliezer's notation is used. In writing the expression for R, Eliezer uses the fact that $\alpha_y' = -\alpha_y$, $(\beta\alpha_y\alpha_z)' = -\beta\alpha_y\alpha_z$, where primes denote the transpose of the matrix. Consequently $\psi'\alpha_y\psi = 0$ and $\psi'\beta\alpha_y\alpha_z\psi = 0$.

‡ This ϕ is not to be confused with ϕ in (8 *a*).

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A FEW SELF-RECIPROCAL FUNCTIONS

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1. The object of this note is to find out a few Self-Reciprocal Functions for Hankel transforms. I denote a function $f(x)$ as R_μ, if it is Self-Reciprocal for Hankel transforms of order μ so that it is given by

$$f(x) = \int_0^\infty J_\mu (xy) f(y) \sqrt{xy}\, dy, \tag{1.1}$$

where $J_\mu(x)$ is a Bessel function of order μ. If $\mu = \frac{1}{2}$, then $f(x)$ is denoted by R_s, while if it is $R - \frac{1}{2}$, it is written as R_c.

Hardy and Titchmarsh[8] have shown that under certain broad conditions $f(x)$ is R_μ, if

$$f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^{s/2}\, \Gamma\left(\frac{1}{4} + \frac{\mu}{2} + \frac{s}{2}\right) \psi(s)\, x^{-s}\, ds, \tag{1.2}$$

where $0 < c < 1$,

and $\psi(s) = \psi(1 - s)$.

If $\psi(s) = -\psi(1 - s)$, then $f(x)$ is denoted by $-R_\mu$ and in that case $f(x)$ is said to be Skew reciprocal for Hankel transforms of order μ.

2. We start with the integral given by Watson[12]

$$\int_0^\infty \frac{J_{\alpha+p}(ax)\, J_{\alpha-p-1}(ax)\, dx}{x^\lambda}$$

$$= \frac{a^{\lambda-1}\, \Gamma\left(\frac{\lambda}{2} + \frac{1}{2}\right) \Gamma\left(\alpha - \frac{\lambda}{2}\right)}{2\, \Gamma\left(p + \frac{\lambda}{2} + 1\right) \Gamma\left(\alpha + \frac{\lambda}{2}\right) \Gamma\left(\frac{\lambda}{2} - p\right)} \tag{2.1}$$

where $\lambda \neq 0$.

Putting $\lambda = (1 - s)$, $d = 3/2$, $p = -\frac{1}{2}$ and $a = 1/\sqrt{2}$, we obtain that

$$\int_0^\infty \left[\mathrm{J}_1\left(\frac{x}{\sqrt{2}}\right)\right]^2 t^{s-1}\, dt = \frac{2^{s/2}}{2} \cdot \frac{1}{\Gamma\left(2 - \frac{s}{2}\right)}, \tag{2·2}$$

where $s \neq 1$.

∴ Applying Mellin's Inversion formula[7] we obtain

$$\left[\mathrm{J}_1\left(\frac{x}{\sqrt{2}}\right)\right]^2 = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^{s/2}\, \Gamma\left(\frac{3}{2} + \frac{s}{2}\right)}{2\, \Gamma\left(2 - \frac{s}{2}\right) \Gamma\left(\frac{3}{2} + \frac{s}{2}\right)} x^{-s}\, ds,$$

$$= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^{s/2}\, \Gamma\left(\frac{3}{2} + \frac{s}{2}\right) \psi(s)\, x^{-s}\, ds, \tag{2·3}$$

where $0 < c < 1$,

and $\psi(s) = \psi(1 - s)$.

Hence from (2·3) and (1·2) we find that

$$\left[\mathrm{J}_1\left(\frac{x}{\sqrt{2}}\right)\right]^2 \tag{2·4}$$

is $\mathrm{R}_{5/2}$.

3. Goldstein[6] has shown that

$$\int_0^\infty t^{(l-1)}\, e^{t/2}\, \mathrm{I}_\nu(2a\sqrt{t})\, \mathrm{W}_{k,m}(t)\, dt$$

$$= \frac{\Gamma\left(\frac{\nu}{2} + l + m + \frac{1}{2}\right) \Gamma\left(\frac{\nu}{2} + l - m + \frac{1}{2}\right)}{\Gamma(\nu + 1)\, \Gamma\left(\frac{\nu}{2} + l - k + 1\right)}$$

$$\times a^\nu\, {}_2\mathrm{F}_2\left[\begin{matrix} \frac{\nu}{2} + l + m + \frac{1}{2},\ \frac{\nu}{2} + l - m + \frac{1}{2}; \\ a^2,\ \nu + 1,\ \frac{\nu}{2} l - k + 1; \end{matrix}\right]$$

where $\left(l + \frac{\nu}{2} - m + \frac{1}{2}\right) > 0.$ (3·1)

Putting

$$k=\frac{p}{2}-\frac{5}{4},\quad m=\frac{p}{2}-\frac{1}{4},\quad \frac{t^2}{2}\text{ for }t\quad\text{and}\quad\frac{a}{\sqrt{2}}\text{ for }a,$$

we find that (3·1), becomes

$$\int_0^\infty (at)^{(2l-1)}\, e^{t^2/4}\, W_{p/2-5/4,\ p/2-1/4}\left(\frac{t^2}{2}\right) I_\nu(at)\, dt$$

$$=\frac{\Gamma\left(\frac{\nu}{2}+l+\frac{p}{2}+\frac{1}{4}\right)\Gamma\left(\frac{\nu}{2}+l-\frac{p}{2}+\frac{3}{4}\right)a^{\nu+2l-1}}{\Gamma(\nu-1)\,\Gamma\left(\frac{\nu}{2}+l-\frac{p}{2}+\frac{9}{4}\right)2^{\nu/2-l+1}}$$

$$\times\ {}_2F_2\left[\begin{matrix}\frac{\nu}{2}+l+\frac{p}{2}+\frac{1}{4},\ \frac{\nu}{2}+l-\frac{p}{2}+\frac{3}{4}\ ;\\ \frac{a^2}{2},\ \nu+1,\ \frac{\nu}{2}+l-\frac{p}{2}+\frac{9}{4}\ ;\end{matrix}\right]$$

where $\left(l+\frac{\nu}{2}-\frac{p}{2}+\frac{3}{4}\right)>0.$ (3.2)

Bailey[5] has shown that

$$e^{t^2/4}\, W_{p/2-5/4,\ p/2-1/4}\left(\frac{t^2}{2}\right) \tag{3.3}$$

is R_p.

Also Dr. Brij Mohan[4] has shown that the kernel

$$x^{1/2(p+q+1)}\, I_{1/2(p-q)}(x), \tag{3.4}$$

transforms R_p into R_q.

Hence putting

$$\left.\begin{aligned}&\tfrac{1}{2}(p+q+1)=2l-1,\\ \text{and}\quad&\tfrac{1}{2}(p-q)=\nu,\\ \text{we find that}\quad&\\ &p=2l+\nu-\tfrac{3}{2},\\ \text{and}\quad&q=2l-\nu-\tfrac{3}{2}\end{aligned}\right\}. \tag{3.5}$$

Applying the results of (3.5), (3.4), and (3.3) to (3.2) we conclude that

$$x^{2\nu+\mu+1/2}\ {}_2F_2\left[\begin{matrix}2\nu+\mu+1,\ \frac{3}{2}\ ;\\ \nu+1,\ \ 3;\end{matrix}\ \frac{x^2}{2},\right] \tag{3.6}$$

is R_μ.

Some of the particular cases of this function are interesting.

Putting $\nu = 1 - \frac{\mu}{2}$, we find that

$$x^{3/2}\,{}_1F_1\left(2-\frac{\mu}{2};\ \frac{3}{2};\ \frac{x^2}{2}\right) \tag{3.7}$$

is R_μ,

Again, putting $\nu = -\mu$, we find that

$$x^{1/2-\mu}\,{}_1F_1\left(\frac{3}{2};\ 3;\ \frac{x^2}{2}\right) \tag{3.8}$$

is R_μ.

4. Miss Sinha[9] has shown that

$$\int_0^\infty x^{(l-1)}\,K_m(ax)\,J_\nu(bx)\,J_\delta(bx)\,dx$$

$$= \frac{2^{l-2}\,b^{\nu+\delta}\,\Gamma\left(\frac{l+\nu+\delta+m}{2}\right)\Gamma\left(\frac{l+\nu+\delta-m}{2}\right)}{a^{l+\nu+\delta}\,\Gamma(\nu+1)\,\Gamma(\delta+1)}$$

$$\times\ {}_4F_3\left[\begin{matrix}\frac{1+\nu+\delta}{2},\ \frac{2+\nu+\delta}{2},\ \frac{l+\nu+\delta+m}{2},\\ \frac{l+\nu+\delta-m}{2};\ \frac{-4b^2}{a^2};\ 1+\nu,\ 1+\delta,\ 1+\nu+\delta;\end{matrix}\right] \tag{4.1}$$

where $\mathrm{R}(l+\nu+\delta\pm m)>0,\ \mathrm{R}(\delta)>-1,$

and $\mathrm{R}(\nu)>-1.$

After adjusting a little, we find that it may be put in the form,

$$\int_0^\infty (ax)^{l+\nu+\delta-1/2}\,K_m(ax)\,\frac{J_\nu(bx)\,J_\delta(bx)}{x^{\nu+\delta+1/2}}\,dx$$

$$= \frac{2^{l-2}\,b^{\nu+\delta}\,\Gamma\left(\frac{\nu+l+\delta+m}{2}\right)\Gamma\left(\frac{\nu+l+\delta-m}{2}\right)}{\sqrt{a}\,\Gamma(\nu+1)\,\Gamma(\delta+1)}$$

$$\times\ {}_4F_3\left[\begin{matrix}\frac{1+\nu+\delta}{2},\ \frac{2+\nu+\delta}{2},\ \frac{l+\nu+\delta+m}{2},\\ \frac{l+\nu+\delta-m}{2};\ \frac{-4b^2}{a^2};\ 1+\nu,\ 1+\delta,\ 1+\nu+\delta;\end{matrix}\right] \tag{4.2}$$

I have shown in a previous paper[11] that

$$\frac{J_\mu(a_1x)\,J_\nu(a_2x)\,\dots\,J_k(a_nx)}{x^{\mu+\nu+\dots+k+1/2}},$$

where $a_1 + a_2 + \dots + a_n$ is finite and $a_1, a_2, \dots, a_n$ are all + ve, is R_1. Hence taking $n = 2$ and $a_1 = a_2 = b_1$ we find that

$$\frac{J_\mu(ax)\,J_\nu(bx)}{x^{\mu+\nu+1/2}} \tag{4.3}$$

is R_1 if b is finite and + ve.

Also Dr. Brij Mohan[1] has shown that the Kernel

$$x^{1/2(\mu+p+1)}\,K_{1/2(p-\mu)}(x), \tag{4.4}$$

transforms R_μ into R_p.

5. Putting $\mu = 1$, we find that the Kernel

$$x^{1/2(p+2)}\,K_{1/2(p-1)}(x) \tag{5.1}$$

transforms R_1 into R_p.

Hence putting

$$\left.\begin{aligned} &\tfrac{1}{2}(p-1) = m,\\ &1 + \frac{p}{2} = l + \nu + \delta - \frac{1}{2},\end{aligned}\right\} \tag{5.2}$$

we find that

$$p = m + l + \nu + \delta - 1 = 2m + 1,$$

and

$$l + \nu + \delta - m = 2.$$

Hence applying the results of (5.6), (5.5) and (5.3) to (5.2), we find that

$$\frac{1}{\sqrt{x}}\,{}_4F_3\left[\begin{matrix}\frac{1+\nu+\delta}{2}, & \frac{2+\nu+\delta}{2}, & 1+m, & 1;\\ \frac{-4b^2}{x^2}; & 1+\nu, & 1+\delta, & 1+\nu+\delta;\end{matrix}\right], \tag{5.3}$$

where $\nu + \delta - m \leq 2$ is R_{2m+1}.

In other words, we find that

$$\frac{1}{\sqrt{x}}\,{}_4F_3\left[\begin{matrix}\frac{1\mp\nu+\delta}{2}, & \frac{2+\nu+\delta}{2}, & \frac{1}{2}+\frac{m}{2}, & 1;\\ \frac{-4b^2}{x^2}; & 1+\nu, & 1+\delta, & 1+\nu+\delta;\end{matrix}\right], \tag{5.4}$$

where $\nu + \delta - \frac{m}{2} \leq \frac{3}{2}$, is R_m.

As a particular case putting $\nu + \delta = 0$, we find that

$$\frac{1}{\sqrt{x}}\, {}_3F_2\left[\frac{1}{2},\ \frac{1}{2}+\frac{m}{2},\ 1;\ 1+\nu,\ 1-\nu;\ \frac{-4b^2}{x^2}\right] \tag{5.5}$$

is R_m if b is + ve and finite.

Further putting $\nu = \frac{1}{2}$, we find that

$$\frac{1}{\sqrt{x}}\, {}_2F_1\left(\frac{1}{2}+\frac{m}{2},\ 1;\ \frac{3}{2};\ \frac{-4b^2}{x^2}\right),$$

is R_m. In particular, if $m = 2$ and $b = \frac{1}{2}$ it reduces to the R_2 function

$$\frac{1}{\sqrt{x}}\, {}_1F_0\left(1;\ -\frac{1}{x^2}\right) = \frac{x^{3/2}}{(x^2+1)}$$

given by me in a previous paper.[12]

6. Macrobert[10] has shown that

$$\sqrt{\frac{\pi}{2}}\, \Gamma(m+n+1)\, \Gamma(m-n)\, (z^2-1)^{-m/2}\, P_n^{-m}(z)$$

$$= \int_0^\infty e^{-\lambda z}\, K_{n+1/2}(\lambda)\, \lambda^{m-1/2}\, d\lambda, \tag{6.1}$$

where $R(z) > -1$, $R(m+n+1) > 0$,

and $R(m-n > 0$.

Putting $n = 0$ and writing $(m+1)$ for m_1, & $(z-1)$ for z we find that (6.1) may be written as

$$\Gamma(m+2)\, \Gamma(m+1)\, (z-2)^{-(m+1)/2}\, P_0^{-(m+1)}(z-1)$$

$$= \sqrt{\frac{2}{\pi}} \int_0^\infty e^{-\lambda z} e^{\lambda}\, K_{1/2}(\lambda)\, (\lambda z)^{m+1/2}\, d\lambda, \tag{6.2}$$

where $R(z) > 0$ and $R(m+1) > 0$.

Now it is known that

$$\sqrt{\frac{2}{\pi}}\, e^z\, K_{1/2}(z) = \frac{1}{\sqrt{z}}. \tag{6·3}$$

Further, Dr. Brij Mohan[3] has shown that the function

$$\frac{1}{\sqrt{z}} \tag{6.4}$$

is R_p. Also, it has been further shown by Dr. Brij Mohan[2] that the Kernel

$$e^{-z} z^{p-1/2} \tag{6.5}$$

transforms R_{p-1} into R_p.

Applying the results of (6.4) and (6.5) to (6.2), we find that the function

$$(z-2)^{-m/2} p_0^{-m} (z-1) = (z-2)^{-m/2}, \tag{6.6}$$

where $P_0^{-m}(z)$ is Associated Legendre Polynomial of the 1st kind is R_m.

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STUDIES IN HETEROCYCLIC N-OXIDES

Part I. Raman Spectra of Pyridine N-Oxide and Its Solutions

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While a number of workers have studied the infra-red absorption spectra of N-oxides of tertiary amines and heterocyclic compounds, information about the Raman spectra of these compounds is relatively scarce. Thus, the only recorded instances on the Raman spectra of tertiary amine N-oxides are by Edsall,[1] Kahovec,[2] and Goubeau and Fromme[3] who have studied the Raman spectrum of trimethylamine N-oxide and have assigned a line in the region of 950 cm.$^{-1}$ to the N—O stretching vibration. The Raman spectra of heterocyclic N-oxides have not been recorded till recently. The present authors[4] studied the Raman spectrum of pyridine N-oxide (II) and assigned a band at 1254 ± 10 cm.$^{-1}$ to the N—O stretching vibration.

Raman effect studies have been extensively used in the demonstration of hydrogen bond formation with the oxygen of carbonyl compounds,[5] but manifestations of the hydrogen bond of the type (N—O- -H) do not appear to have been studied by this method. Raman spectra of pyridine N-oxide (II) in mixtures of phenol, methanol and dioxan have been recorded in the present communication with a view to studying the (N—O- -H) manifestations.

Experimental

Pyridine N-oxide was prepared by the method of Ochiai[6] and purified through vacuum distillation. Phenol, methanol and dioxan of high grade purity were employed. A Hilger Raman source and a Fuess glass spectrograph with a dispersion of 19 cm.$^{-1}$ in the region of 4358 Å were used. 4358 Å was used as the exciting line and Hartmann diaphragm to measure the shifts of the order of a few wave numbers. As (II) is a low-melting solid, the outflowing water from the Hilger Raman source was maintained at a temperature just high enough to keep (II) in molten state.

Results

The Raman frequencies of pyridine (I) and pyridine N-oxide (II) as recorded by the authors are given in Table I. The frequencies of (I) are in

good agreement with those reported earlier by Kline and Turkevich,[7] Corrsin, Fax and Lord,[8] and Puranik and Jaya Rao.[9]

TABLE I

Raman frequencies of pyridine and pyridine N-oxide

Pyridine cm.$^{-1}$	Pyridine N→O cm.$^{-1}$	Pyridine cm.$^{-1}$	Pyridine N→O cm.$^{-1}$
	186 (1 *b*)		1254±10 (3 *b*)
		1284 (2 *b*)	
	232 (1 *b*)		1382 (2)
407 (1 *b*)		1473 (2)	
	520 (1)		1509 (1)
	553 (1)		1558 (1)
		1578 (5)	
	596 (2)		
602 (1 *b*)		1597 (2)	
	624 (1)		1613 (8)
653 (3)			
	686 (4)		1893 (2 *b*)
	730 (1)		2034 (2)
	767 (6)		2100 (1)
	841 (1 *b*)		2233 (1)
842 (1)		2455 (1 *b*)	
888 (2)		2494 (2 *b*)	
			2495 (2)
933 (3)			
			2826 (1)
974 (1)		2872 (2 *b*)	
	989 (1)		2874 (2)
990 (8)		2913 (2)	
	1017 (3)		2918 (3)
1026 (8)		2954 (2)	2954 (1)
	1050 (3)		
1067 (1 *b*)		2990 (2)	
	1104 (1)		
1143 (1 *b*)		3022 (1)	
	1157 (2 *b*)		3046 (4)
1214 (2 *b*)	1217 (3)	3053 (8)	
			3086 (1)

Changes in the relevant and important frequencies of the pyridine ring as well as the N—O stretching vibrations in mixtures of (II) with phenol, methanol and dioxan in the proportions of 1 : 1, 1 : 2 and 1 : 4 by volume in each solvent have been recorded and the results are listed in Table II.

TABLE II

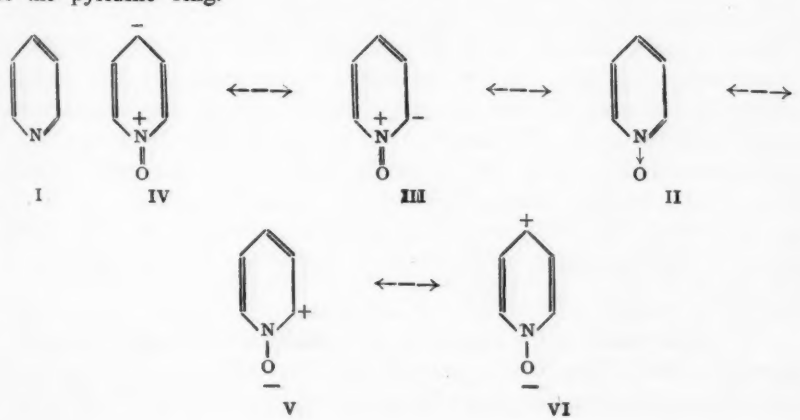
Raman frequencies of pyridine N-oxide in solutions

Assignment	Pyridine cm.$^{-1}$	Pyridine N-oxide cm.$^{-1}$	Pyridine N-oxide and phenol			Pyridine N-oxide and methanol			Pyridine N-oxide and dioxan		
			1 : 1 cm.$^{-1}$	1 : 2 cm.$^{-1}$	1 : 4 cm.$^{-1}$	1 : 1 cm.$^{-1}$	1 : 2 cm.$^{-1}$	1 : 4 cm.$^{-1}$	1 : 1 cm.$^{-1}$	1 : 2 cm.$^{-1}$	1 : 4 cm.$^{-1}$
N→O	..	1254±10	1270	1270	1266	1266	1269	1265	1254±10	1254±10	1254±10
C=N	1578	1558	1558	1558	1558	1558	1558	1558	1558	1558	1558
C=C	1597	1613	1620	1618	1618	1615	1617	1617	1613	1613	1613

ASSIGNMENT OF LINES

As the double bonds are more amenable to electronic changes than others, attention has been restricted to the double bond frequencies of the pyridine ring, and to the assignment of a band to the N—O stretching vibration.

The earlier workers[7, 8, 9] have analysed and assigned most of the lines of pyridine to different modes of ring vibrations; thus the lines at 1578 cm.$^{-1}$ and 1597 cm.$^{-1}$ have been assigned respectively to the C=N and C=C bonds of the pyridine ring.[9]



By a scrutiny of the spectra of (I) and (II) the band at 1254 ± 10 cm.$^{-1}$ has been assigned by the authors to the N—O stretching vibration. The various canonical forms (III–VI)[6] that are possible in (II) would give to the N—O bond considerable double bond character and hence our assignment at 1254 ± 10 cm.$^{-1}$ to this bond. This agrees well with the infra-red absorption spectra of Blasina and co-workers[10] who have assigned a band at 1242 cm.$^{-1}$ to the N—O stretching vibration of (II) in solid and liquid states, and Wiley and Slaymaker[11] who have placed a band in the region of 1266 cm.$^{-1}$ for the same bond. The difference in our assignment from those of Edsall,[1] Kahovec[2] and Goubeau and Fromme[3] is understandable on the basis of the well-known differences in the physical and chemical properties of heterocyclic N-oxides from tertiary amine N-oxides. Our assignment also appears to be confirmed by the shift the band undergoes in mixtures of acceptor solvents.

In the region of 1550 cm.$^{-1}$ to 1650 cm.$^{-1}$ the authors have recorded two lines, one at 1558 cm.$^{-1}$ and another at 1613 cm.$^{-1}$ The former has been assigned to C=N and the latter to C=C bonds. In (II) the presence of an oxygen atom tending to pull electrons away from the nitrogen creates a small, but definite influence towards the weakening of the C=N bond. This is indicated in the lowering of the C=N frequency from 1578 cm.$^{-1}$ in (I) to 1558 cm.$^{-1}$ in (II). All the possible canonical forms of (II) also tend to weaken considerably the double bond character of the C=N bond.

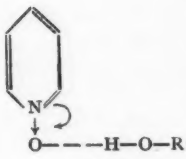
DISCUSSION OF RESULTS

A comparison of the spectra of (I) and (II) reveals clearly that most of the Raman lines of (I) are altered when it is converted into (II). In addition, in (II) there are a few new lines also, out of which one has now been assigned to N→O stretching vibration. The considerable alteration of the lines of (I) indicate a severe disturbance in the geometry of the original substance on its conversion into (II). This is obviously a consequence of the N→O bond utilising the lone pair of electrons of the tertiary nitrogen, and thus creating a positive charge on it. This causes a pull on the electrons from the attached double bond and the ring. The lowering of the C=N frequency by about 20 cm.$^{-1}$ is a marked effect. This finds a chemical confirmation in the reactivity of the 2-methyl group in nucleophilic condensation with diethyl oxalate, a reaction which is facilitated in 2-picoline N-oxide but not in 2-picoline.[12]

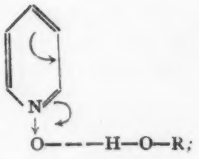
An enhancement in the frequency of C=C by about 15 cm.$^{-1}$ is another important effect of the N-oxide bond formation. This can be explained on the basis that the aromatic properties of the original pyridine ring have been

diminished; as a consequence, the ethylenic double bond characters become more prominent.

In a solution of the N-oxide (II) in neutral solvents like carbon tetrachloride no changes in the Raman lines were observed. However, on mixing (II) with acceptor solvents like phenol and methanol, changes in Raman lines are found to occur and these should be attributed to the formation of hydrogen bonds. In the earlier studies on the formation of hydrogen bonds with carbonyl compounds and the hydroxylic substances mentioned above, the C=O frequency was markedly diminished and both the original and new frequencies were found in many cases.[5] In the case of N-oxide, however, there is an enhancement in the N→O frequency by about 15 cm.$^{-1}$ indicating a strengthening of the bond. This may be well explained if one visualises, that in the presence of acceptor molecules environing the N-oxide group, electrons are drawn towards the N→O group through electromeric polarisation, thus enhancing the strength of this bond as indicated in the following schemes:



(A)



(B)

The above observation finds a parallel, though caused by a mechanism exactly opposite of the present one, in the results of Katritzky and his co-workers.[13, 14] They studied the infra-red absorption spectra of a number of 2- and 4-substituted pyridine N-oxides and showed that the electron-attracting groups in either of the positions tend to enhance the N→O frequency.

The Raman spectra of (II) with donor solvents like dioxan do not show any change. This is not unexpected as there is no possibility of hydrogen bond formation in these cases.

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SUMMARY

The Raman spectra of pyridine N-oxide and its solutions in phenol, methanol and dioxan have been recorded. The band at 1254 ± 10 cm.$^{-1}$ has been assigned to the N—O stretching vibration. The variations in the double bond frequencies of pyridine ring, and in the frequency of N—O bond, owing to hydrogen bond formation, have been listed. On conversion of pyridine to pyridine N-oxide the various frequencies attributed to the different modes of vibrations in the pyridine ring get altered as a result of the considerable disturbance caused by the new bond.

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SYNTHESIS OF 6:7:3′:4′-TETRAMETHOXY ISOFLAVONE

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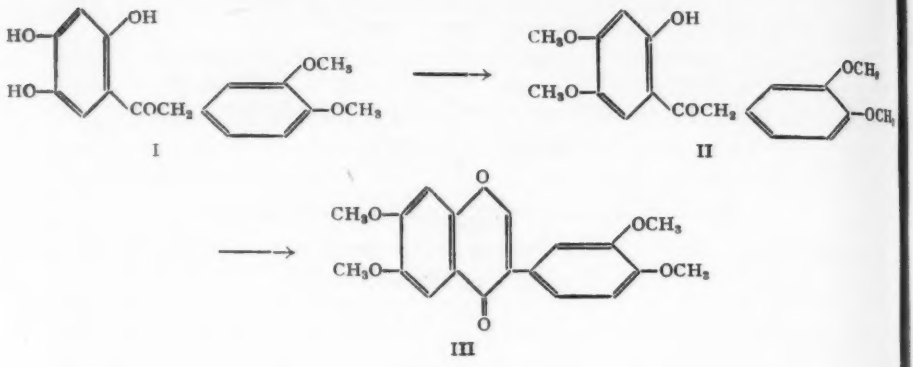
Maxima Substance A was isolated from the roots of *Tephrosia maxima*[1] and assigned the structure 6:7:3′:4′-dimethylene-dioxy isoflavone.[2] For confirmation of this structure, 6:7:3′:4′-tetramethoxy isoflavone was required as a reference sample. This has now been prepared employing the following procedure:—

Adopting the method of Edwards[3] for the preparation of homopiperonitrile, 3:4-dimethoxyphenyl pyruvic acid[4] was converted through its oxime into 3:4-dimethoxyphenyl acetonitrile.[5] This was condensed with hydroxyquinol[6] (Hoesch reaction) to yield 2:4:5-trihydroxyphenyl-3:4-dimethoxy benzyl ketone (I). This ketone on methylation with dimethylsulphate and anhydrous potassium carbonate in acetone medium yielded 2-hydroxy-4:5:3′:4′-tetramethoxy desoxybenzoin (II). The same desoxybenzoin was also obtained by the interaction of the trimethyl ether of hydroxy-quinol and homoveratroyl chloride[7, 8] in the presence of anhydrous aluminium chloride (Friedel and Crafts reaction). During this reaction the methoxyl group in the hydroxyquinol nucleus which is *ortho* to the entrant carbonyl group underwent smooth demethylation to yield the desired *ortho*-hydroxy desoxy-benzoin (II) (*cf.*, Ballio and Pocchiari[9]). The trimethyl ether of hydroxyquinol (V) required in this connection was prepared by (i) the methylation of hydroxyhydroquinone triacetate with alkali and dimethylsulphate[10] and (ii) by the oxidation of vanillin with hydrogen peroxide in alkaline medium[11] followed by methylation with dimethylsulphate. Samples of desoxybenzoin obtained by both the methods were identical in their melting points, colour reactions and solubility behaviour. The desoxybenzoin was smoothly converted into 6:7:3′:4′-tetramethoxy isoflavone (III) by treatment with ethylformate in the presence of powdered sodium at 0°.[12]



EXPERIMENTAL

2:4:5-Trihydroxyphenyl 3 : 4-dimethoxybenzyl ketone

(*a*) *By Hoesch Reaction.*—To a solution of hydroxyquinol (10·5 g.) and 3:4-dimethoxyphenyl acetonitrile (10·7 g.) in absolute ether (50 c.c.) freshly fused zinc chloride (2 g.) was added. The mixture was cooled to 0° and dry hydrogen chloride gas was passed through it for 5 hours, rapidly during the first half an hour and at a moderate rate subsequently. The mixture was kept well-corked in an ice-chest for 48–72 hours. The ether layer was decanted off from the dark-green oily layer which was subsequently washed with fresh lots of absolute ether. Water (25 c.c.) was added and the solution containing the iminohydrochloride was heated in a boiling water-bath for two hours. The dark-brown solid that separated was filtered and crystallised from dilute alcohol and subsequently from ethyl acetate- petroleum ether. The ketone was obtained as rhombs, m.p. 189–91° (Yield 0·25 g.). It gave an olive-green colour with alcoholic ferric chloride. It was soluble in aqueous sodium hydroxide giving an yellow solution changing over to orange-red and finally to reddish brown. It was soluble in aqueous sodium bicarbonate giving pale-yellow solutions (Found: C, 63·6; H, 4·6%; $C_{16}H_{16}O_6$ requires C, 63·2; H, 5·3%). The 2 : 4-dinitrophenylhydrazone of the phenolic ketone was prepared by refluxing the substance (25 mg. in 1 c.c. alcohol) with 2:4-dinitrophenylhdyrazine (20 mg. in 5 c.c. alcohol) and a few drops of concentrated hydrochloric acid. The red solid obtained on working up the reaction product was crystallised from ethyl acetate-petroleum ether. It was obtained as rods, m.p. 207–08° (Found: C, 54·1; H, 4·5%; $C_{22}H_{20}O_9N_4$ requires C, 54·6; H, 4·1%).

2-Hydroxy-4:5:3′:4′-tetramethoxy desoxy benzoin

2:4:5-Trihydroxyphenyl-3:4-dimethoxy benzyl ketone (1·0 g.) dissolved in dry acetone (150 c.c.) was refluxed with dimethyl sulphate (2 c.c.) (excess) and anhydrous potassium carbonate (4·0 g.) for 8 hours. The potassium salts were filtered off and washed with warm acetone (2×20 c.c.). The solvent was distilled off from the filtrate and the pale-yellow residue obtained was treated with 5% aqueous sodium bicarbonate to remove the unreacted ketone. The pale-yellow tetramethyl ether was filtered and crystallised first from alcohol and subsequently from benzene-petroleum ether. Colourless thin rods, m.p. 135–137°, were obtained (Yield 0·7 g.). The substance gave an emerald-green colour with alcoholic ferric chloride. It was soluble in aqueous sodium hydroxide giving a pale-yellow solution. It was insoluble in aqueous sodium carbonate. (Found: C, 65·5; H, 6·3; OCH_3, 35·6%. $C_{18}H_{20}O_6$ requires C, 65·1; H, 6·0; OCH_3, 37·4%.)

(*b*) *By Friedel and Crafts Reaction.*—Homoveratroyl chloride (15·0 g.) was dissolved in absolute ether (150 c.c.) and treated with hydroxyquinol trimethyl ether (12·0 g.) in ether (50 c.c.). Then anhydrous aluminium chloride (20·0 g.) was carefully added in small amounts. The contents were refluxed over a water-bath for 8 hours. After cooling, the ether layer was separated and the reddish-brown aluminium chloride complex decomposed by the addition of hydrochloric acid (1:2; 90 c.c.) and heating on the steam-bath for an hour. The aqueous solution was extracted with ether and combined with the original ether layer. The combined ether extract was washed with hydrochloric acid (1:2; 20 c.c.) and with water (20 c.c.). The ether layer was extracted twice with 10% aqueous sodium hydroxide. The aqueous alkaline extract was acidified carefully with concentrated hydrochloric acid and repeatedly extracted with ether. The ether layer was washed with water, dried over anhydrous magnesium sulphate and distilled. The dark-brown residue was macerated with alcohol (5–10 c.c.). The pale-yellow solid that separated was filtered and crystallised from benzene-petroleum ether when 2-hydroxy-4:5:3′:4′-tetramethoxy desoxybenzoin was obtained as colourless thin rods, m.p. 136–38° (Yield 2·0 g.). It gave an emerald-green colour with alcoholic ferric chloride. It did not depress the melting point of the ketone obtained by the Hoesch condensation of hydroxy quinol and 3:4-dimethoxy acetonitrile (Found: C, 65·5; H, 6·1%; $C_{18}H_{20}O_6$ requires C, 65·1; H, 6·0%).

6:7:3′:4′*-Tetramethoxy isoflavone*

A solution of 2-hydroxy-4:5:3′:4′-tetramethoxy desoxybenzoin (0·4 g.) in freshly distilled ethyl formate (15 c.c.) was cooled to 0° and added in small

portions with stirring to powdered sodium (0·4 g.). The mixture was stirred for an hour more keeping the flask in ice-salt mixture. The flask was corked and left in the ice-chest for two days. Pieces of ice and concentrated hydrochloric acid (10 c.c.) were added to the mixture with stirring. The flask was then corked and left overnight at room temperature. Unreacted ethylformate was removed by distillation under reduced pressure. The solid that separated on cooling was filtered, macerated with cold alcohol and again filtered. It was then crystallised twice from rectified spirit. The tetramethoxy isoflavone was obtained as colourless rectangular prisms, m.p. 188–89° (Yield 100 mg.). It did not give any colour with alcoholic ferric chloride. It was insoluble in sodium hydroxide, sodium carbonate and sodium bicarbonate solutions (Found: C, 66·4; H, 5·6; OCH_3, 34·7%; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3; OCH_3, 36·2%).

SUMMARY

The synthesis of 6:7:3′:4′-tetramethoxy isoflavone is described.

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